Radical Deoxychlorination of Cesium Oxalates for the Synthesis of Alkyl Chlorides

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Supporting Information

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1. Materials and Methods

Unless otherwise stated, reactions were performed under a nitrogen atmosphere using freshly dried solvents. Methylene chloride (CH_2Cl_2), diethyl ether (Et_2O), tetrahydrofuran (THF), and 1,4-dioxane were dried by passing through activated alumina columns. Ethyl trichloroacetate (Sigma Aldrich 163155) was distilled prior to use and stored in a Schlenk tube under an atmosphere of nitrogen. Triethylamine (Et_3N) was distilled over calcium hydride prior to use. Selectfluor was used as received, and was stored in the freezer of a nitrogen-filled glovebox. Dimethyl 2,2-dichloromalonate was prepared according to literature procedure.[1] All other commercially obtained reagents were used as received unless specifically indicated. Halogenation reactions were performed in a Hepatochem EvoluChem™ PhotoRedOx Box device and irradiated with a Kessil A160WE blue LED lamp. Cooling with the internal fan afforded reaction temperatures of 27 °C, as measured with a thermocouple. Unless otherwise stated, reactions were stirred at a rate of 430 rpm. Reaction screens in 1 dram vials were performed with a Biotage 355543 stir bar, while those in a ½ dram vial utilized a V&P Scientific VP 774-7 stir bar. Chlorination reactions in 20 mL scintillation vials were performed with an egg-shaped stir bar (VWR 58949-010). Bromination and fluorination reactions in 20 mL scintillation vials were performed with a "+"-shaped stir bar (VWR 58947-822) for better stirring with added Cs_2CO_3. All reactions were monitored by thin-layer chromatography using EMD/Merck silica gel 60 F254 pre-coated plates (0.25 mm). Silica gel column chromatography was performed as described by Still et al. (W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem*. **1978**, *43*, 2923–2925) using silica gel (particle size 0.032–0.063) purchased from Silicycle. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 500 (at 500 MHz and 125 MHz respectively) or a Bruker Avance III HD with Prodigy cyroprobe (at 400 MHz and 101 MHz respectively). NMR data is reported relative to internal chloroform, DMSO, or methanol solvent peaks (with respect to TMS (tetramethylsilane)): $CDCl_3$, ^1H, δ = 7.26, ^{13}C, δ = 77.16; DMSO-d_6, ^1H, δ = 2.50, ^{13}C, δ = 39.52; CD_3OD, ^1H, δ = 3.31, ^{13}C, δ = 49.00). NMR data in D_2O is reported relative to DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid): D_2O, ^1H, δ = 4.79. ^{19}F spectra were recorded on a Varian 400 MR spectrometer (at 376 MHz); chemical shifts are reported in parts per million and are referenced to $CFCl_3$ (δ 0 ppm). NMR data are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). HRMS were acquired using either an Agilent 6200 Series TOF with an Agilent G1978A Multimode source using electrospray ionization (ESI) or from the Caltech Mass Spectral Facility using electrospray ionization (ESI), electron ionization (EI), or fast atom bombardment (FAB). GC-Flame ionization detection analysis was performed on

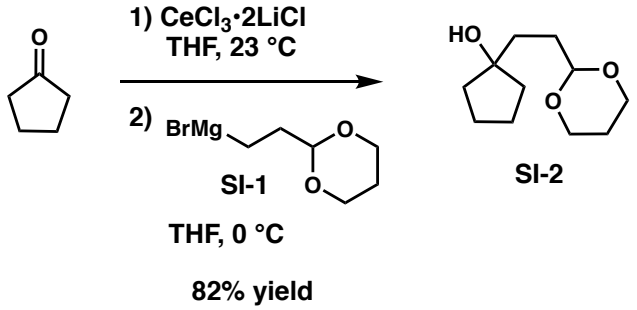
a Agilent Technologies 6850 Network GC system using a Agilent HP-1 capillary column (19091Z-413E: length 30 m, diameter 0.320 mm, film 0.25 μm).

Abbreviations used: Et_2O – diethyl ether; PhMe – toluene; EtOAc – ethyl acetate; THF – tetrahydrofuran; Et_3N – triethylamine; DMAP – 4-dimethylaminopyridine; ETCA – ethyl trichloroacetate.

2. Substrate Preparation

Known cesium oxalates: Substrates **1a**, **1e**, **1i**, **1j**, and **1l** were prepared according to literature procedures and the NMR data were consistent with those reported in the literature.[2]

a. Preparation of cesium 2-((1-(2-(1,3-dioxan-2-yl)ethyl)cyclopentyl)oxy)-2-oxoacetate (1b)



1-(2-(1,3-dioxan-2-yl)ethyl)cyclopentan-1-ol (SI-2): A flame-dried 25 mL round bottom flask was charged with cyclopentanone (100 mg, 1.19 mmol) and put under an atmosphere of argon. A solution of $CeCl_3$•2LiCl[3] (4 mL, 1.19 mmol, 0.3 M in THF, 1.0 equiv) was added at 23 °C, and the pale yellow mixture stirred for 1 h. The mixture was then cooled to 0 °C and Grignard **SI-1**[4] (3.2 mL, 1.19 mmol, 0.37 M in THF, 1.0 equiv) was added dropwise. After 15 min, TLC analysis indicated full conversion, and the mixture was quenched with a saturated aqueous solution of NH_4Cl (3 mL) and stirred at 0 °C for 5 min. H_2O (7 mL) and EtOAc (5 mL) were added and the mixture warmed to room temperature and transferred to a separatory funnel. A saturated aqueous solution of Rochelle's salt (10 mL) was added, after which the aqueous layer was extracted with EtOAc (4 x 15 mL). The combined organic layers were washed with a saturated aqueous solution of NaCl (1 x 15 mL), and the aqueous layer back-extracted with EtOAc (1 x 10 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (5–50% EtOAc/hexanes) to afford tertiary alcohol **SI-2** (195 mg, 82% yield) as a clear oil.

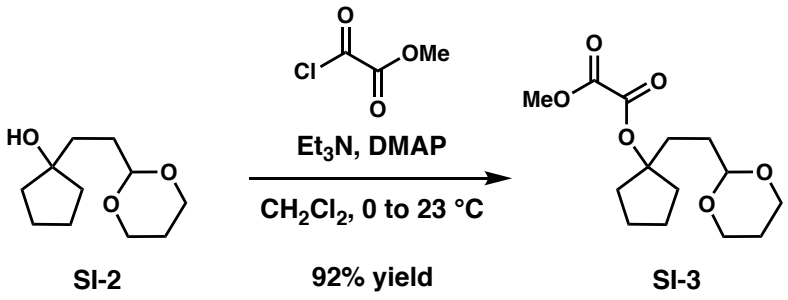
TLC R_f = 0.32 (50% EtOAc/hexanes, *p*-anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.58 (t, *J* = 4.6 Hz, 1H), 4.11 (ddt, *J* = 10.5, 5.0, 1.2 Hz, 2H), 3.83 – 3.72 (m, 2H), 2.15 – 2.01 (m, 1H), 2.08 (s, 1H), 1.78 (dddd, *J* = 7.6, 5.6, 4.5, 1.7 Hz, 4H), 1.71 (ddd, *J* = 8.3, 6.1, 1.8 Hz, 2H), 1.68 – 1.57 (m, 4H), 1.57 – 1.48 (m, 2H), 1.34 (dtt, *J* = 13.5, 2.5, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 102.5, 81.8, 66.9, 39.7, 35.4, 30.8, 25.7, 23.8.

FTIR (NaCl, thin film, cm^{-1}): 3450, 2959, 2852, 1378, 1240, 1145, 994.

HRMS (EI, *m/z*): calc'd for $C_{11}H_{20}O_3$ $(M+\cdot)^+$: 200.1413, found: 200.1411.



1-(2-(1,3-dioxan-2-yl)ethyl)cyclopentyl methyl oxalate (SI-3): To a 50 mL round bottom flask containing a solution of alcohol **SI-2** (146 mg, 0.73 mmol) in CH_2Cl_2 (6.6 mL) at 0 °C was added Et_3N (150 µL, 1.09 mmol, 1.5 equiv), DMAP (9 mg, 0.073 mmol, 0.1 equiv), and methyl oxalyl chloride (80 µL, 1.17 mmol, 1.2 equiv) dropwise by syringe. The reaction was stirred at room temperature for 2.5 h followed by the addition of H_2O (4 mL). The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (4 x 6 mL). The combined organic extracts were washed with a saturated aqueous solution of NaCl (2 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (10–33% EtOAc/hexanes) to afford methyl oxalate **SI-3** (193 mg, 92% yield) as a clear colorless oil.

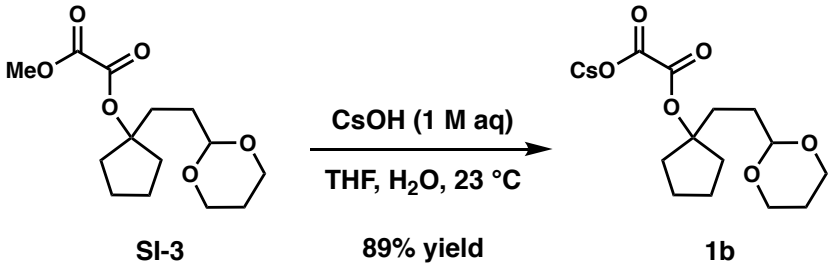
TLC R_f = 0.27 (20% EtOAc/hexanes, *p*-anisaldehyde).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.48 (t, *J* = 5.2 Hz, 1H), 4.07 (ddt, *J* = 10.5, 5.0, 1.4 Hz, 2H), 3.84 (s, 3H), 3.72 (dddd, *J* = 11.9, 10.5, 2.6, 1.6 Hz, 2H), 2.25 – 2.15 (m, 2H), 2.14 – 2.08 (m, 2H), 2.08 – 1.99 (m, 1H), 1.80 – 1.69 (m, 4H), 1.67 – 1.57 (m, 4H), 1.32 (dtt, *J* = 13.5, 2.7, 1.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 157.0, 102.0, 97.1, 67.0, 53.4, 37.4, 31.1, 30.3, 25.9, 24.0.

FTIR (NaCl, thin film, cm^{-1}): 2960, 2853, 2733, 2658, 1766, 1739, 1454, 1332, 1202, 1146, 1079, 997.

HRMS (FAB+, *m/z*): calc'd for $C_{14}H_{21}O_6$ $(M+H-H_2)^+$: 285.1338, found: 285.1317.



cesium 2-((1-(2-(1,3-dioxan-2-yl)ethyl)cyclopentyl)oxy)-2-oxoacetate (1b): A 20 mL scintillation vial was charged with methyl oxalate **SI-3** (119 mg, 0.42 mmol), THF (2.6 mL), and

H_2O (0.27 mL). A 1 M aqueous solution of CsOH (0.420 mL, 0.42 mmol, 1.0 equiv) was then added dropwise to the solution with vigorous stirring. After the addition was complete, the solution was stirred for an additional 5 min. The reaction was concentrated under reduced pressure to remove the THF and the aqueous layer was washed 1:1 pentane/Et_2O (4 x 2 mL). The aqueous layer was then concentrated using rotary evaporation followed by high vacuum (~50 mTorr) to deliver cesium oxalate **1b** as a white amorphous solid (149 mg, 89% yield).

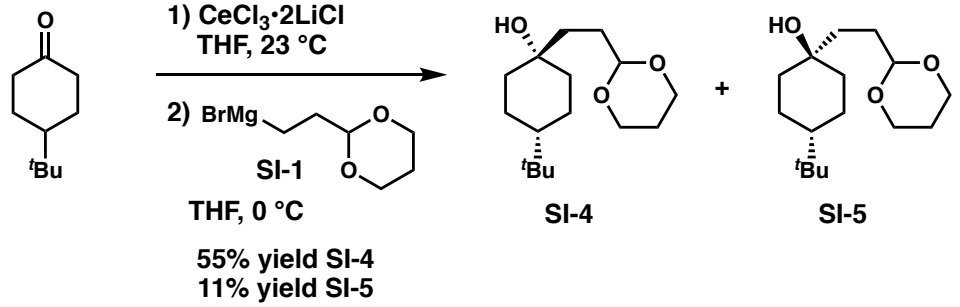
^{1}H NMR (400 MHz, CD_3OD) δ 4.54 (t, *J* = 5.1 Hz, 1H), 4.03 (ddt, *J* = 10.4, 4.9, 1.4 Hz, 2H), 3.83 – 3.69 (m, 2H), 2.28 – 2.13 (m, 2H), 2.12 – 2.05 (m, 2H), 1.98 (dtt, *J* = 13.4, 12.5, 5.0 Hz, 1H), 1.84 – 1.67 (m, 4H), 1.67 – 1.53 (m, 4H), 1.34 (dtt, *J* = 13.4, 2.7, 1.4 Hz, 1H).

^{13}C NMR (101 MHz, CD_3OD) δ 166.3, 166.1, 103.4, 94.9, 67.8, 38.5, 32.3, 31.3, 27.0, 24.9.

FTIR (NaCl, thin film, cm^{-1}): 2960, 2856, 1715, 1645, 1455, 1404, 1200, 1145, 1078, 995.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{13}H_{19}O_6^-$ $(M–Cs)^-$: 271.1187, found: 271.1187.

b. Preparation of cesium *cis*-2-((1-(2-(1,3-dioxan-2-yl)ethyl)-4-(*tert*-butyl)cyclohexyl)oxy)-2-oxoacetate (1c)



***cis*-1-(2-(1,3-dioxan-2-yl)ethyl)-4-(*tert*-butyl)cyclohexan-1-ol (SI-4) and *trans*-1-(2-(1,3-dioxan-2-yl)ethyl)-4-(*tert*-butyl)cyclohexan-1-ol (SI-5):** A flame-dried 100 mL round bottom flask was charged with 4-*tert*-butylcyclohexanone (306 mg, 1.98 mmol) and placed under an atmosphere of argon. A solution of $CeCl_3$•2LiCl[3] (6.6 mL, 1.98 mmol, 0.3 M in THF, 1.0 equiv) was added at room temperature and the pale yellow solution was stirred for 1 h. The mixture was then cooled to 0 ºC and a solution of Grignard reagent **SI-1**[4] (5.0 mL, 2.18 mmol, 0.44 M in THF, 1.1 equiv) was added dropwise. The reaction was stirred at 0 °C for 1 h. A saturated aqueous solution of NH_4Cl (10 mL) was added and the reaction was stirred for 25 min while warming to room temperature. A saturated aqueous solution of Rochelle's salt (5 mL) was added and the aqueous layer was extracted with Et_2O (3 x 12 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (10–50% EtOAc/hexanes) to afford alcohol **SI-4** (295 mg, 55% yield) as a white solid and alcohol **SI-5** (60 mg, 11% yield) as a white solid.

***cis*-1-(2-(1,3-dioxan-2-yl)ethyl)-4-(*tert*-butyl)cyclohexan-1-ol (SI-4):**

TLC R_f = 0.31 (40% EtOAc/hexanes, $KMnO_4$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.53 (t, *J* = 4.9 Hz, 1H), 4.08 (ddt, *J* = 10.4, 5.0, 1.4 Hz, 2H), 3.74 (dddd, *J* = 11.9, 10.5, 2.6, 1.6 Hz, 2H), 2.06 (dtt, *J* = 13.5, 12.5, 5.0 Hz, 1H), 1.88 (br s, 1H), 1.78 – 1.61 (m, 4H), 1.60 – 1.42 (m, 4H), 1.40 – 1.16 (m, 5H), 0.99 – 0.86 (m, 1H), 0.83 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 102.8, 69.9, 67.0, 48.1, 38.0, 37.7, 32.5, 29.1, 27.7, 25.8, 22.6.

FTIR (NaCl, thin film, cm^{-1}): 3481, 2949, 2847, 2732, 2654, 1456, 1432, 1402, 1365, 1242, 1145, 1073, 1006, 979.

HRMS (FAB+, *m/z*): calc'd for $C_{16}H_{29}O_3$ $(M+H-H_2)^+$: 269.2117, found: 269.2095.

***trans*-1-(2-(1,3-dioxan-2-yl)ethyl)-4-(*tert*-butyl)cyclohexan-1-ol (SI-5):**

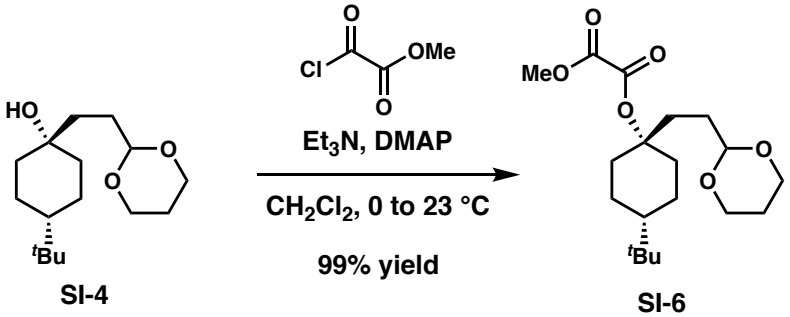
TLC R_f = 0.18 (40% EtOAc/hexanes, $KMnO_4$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (t, *J* = 4.7 Hz, 1H), 4.10 (ddt, *J* = 10.4, 5.0, 1.4 Hz, 2H), 3.76 (dddd, *J* = 11.9, 10.5, 2.6, 1.6 Hz, 2H), 2.17 (br s, *J* = 3.4 Hz, 1H), 2.08 (dtt, *J* = 13.5, 12.5, 5.0 Hz, 1H), 1.77 (ddd, *J* = 13.8, 3.9, 2.2 Hz, 2H), 1.74 – 1.58 (m, 6H), 1.42 – 1.30 (m, 3H), 1.12 – 0.98 (m, 3H), 0.84 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 102.8, 71.5, 67.0, 47.7, 38.8, 32.4, 30.3, 28.8, 27.8, 25.8, 24.5.

FTIR (NaCl, thin film, cm^{-1}): 3296, 2941, 2863, 2729, 2656, 1455, 1365, 1283, 1239, 1211, 1148, 1102, 1007, 984.

HRMS (FAB+, *m/z*): calc'd for $C_{16}H_{29}O_3$ $(M+H-H_2)^+$: 269.2117, found: 269.2123.



***cis*-1-(2-(1,3-dioxan-2-yl)ethyl)-4-(*tert*-butyl)cyclohexyl methyl oxalate (SI-6):** To a 50 mL round bottom flask containing a solution of alcohol **SI-4** (231 mg, 0.85 mmol) in CH_2Cl_2 (7.8 mL) at 0 °C was added Et_3N (0.18 mL, 1.28 mmol, 1.5 equiv), DMAP (10 mg, 0.09 mmol, 0.1 equiv), and methyl oxalyl chloride (0.09 mL, 1.03 mmol, 1.2 equiv) dropwise via syringe. The reaction was stirred at room temperature for 3 h followed by the addition of a 1:1 mixture of a saturated aqueous solution of NaCl and H_2O (3 mL). The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (10–20% EtOAc/hexanes) to give methyl oxalate **SI-6** (301 mg, 99% yield) as a pale yellow oil.

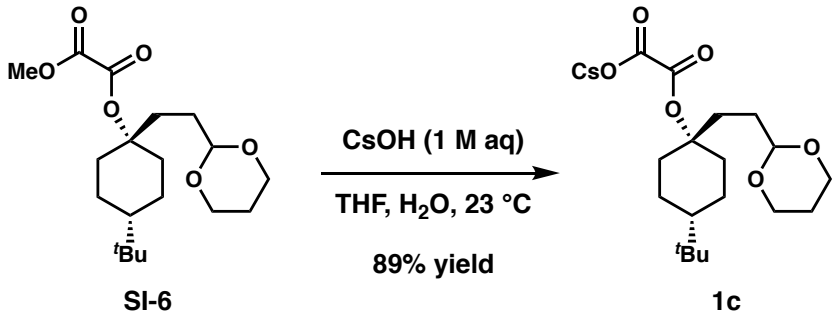
TLC R_f = 0.56 (40% EtOAc/hexanes, UV, $KMnO_4$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47 (t, *J* = 5.2 Hz, 1H), 4.07 (ddt, *J* = 10.4, 5.0, 1.4 Hz, 2H), 3.85 (s, 3H), 3.72 (dddd, *J* = 11.9, 10.5, 2.6, 1.6 Hz, 2H), 2.49 – 2.37 (m, 2H), 2.13 – 1.95 (m, 3H), 1.68 – 1.51 (m, 4H), 1.40 – 1.16 (m, 6H), 1.09 – 0.94 (m, 1H), 0.83 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 156.7, 102.2, 88.1, 67.0, 53.3, 47.2, 34.6, 32.5, 32.4, 29.1, 27.6, 25.9, 22.3.

FTIR (NaCl, thin film, cm^{-1}): 2954, 2866, 2732, 2658, 1767, 1740, 1453, 1366, 1331, 1205, 1165, 1004, 977.

HRMS (FAB+, *m/z*): calc'd for $C_{19}H_{31}O_6$ $(M+H-H_2)^+$: 355.2121, found: 355.2133.



SI-6 1c

cesium *cis*-2-((1-(2-(1,3-dioxan-2-yl)ethyl)-4-(*tert*-butyl)cyclohexyl)oxy)-2-oxoacetate (1c): A 20 mL scintillation vial was charged with methyl oxalate **SI-6** (118 mg, 0.33 mmol), THF (2.1 mL), and H_2O (0.22 mL). A 1 M aqueous solution of CsOH (0.33 mL, 0.33 mmol, 1.0 equiv) was then added dropwise to the solution with vigorous stirring. After the addition was complete, the mixture was stirred for an additional 5 min. The reaction was then concentrated under reduced pressure to remove the THF and the aqueous layer was washed with 1:1 pentane/Et_2O (4 x 2 mL). The aqueous layer was then concentrated under reduced pressure using rotary evaporation followed by high vacuum (~50 mTorr) to afford cesium oxalate **1c** as a white solid (141 mg, 90% yield).

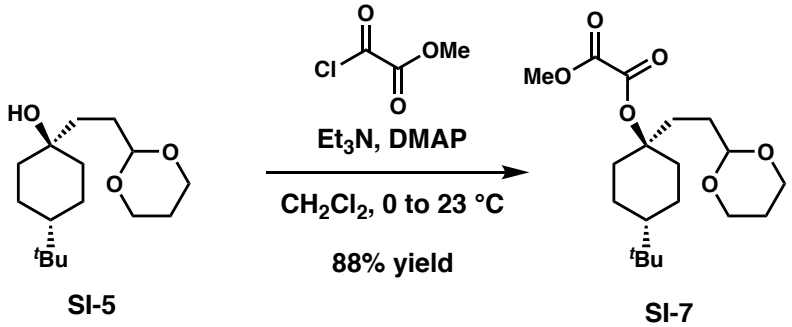
^{1}H NMR (400 MHz, CD_3OD) δ 4.51 (t, J = 5.1 Hz, 1H), 4.02 (ddt, J = 10.4, 5.0, 1.4 Hz, 2H), 3.83 – 3.69 (m, 2H), 2.52 – 2.39 (m, 2H), 2.04 – 1.91 (m, 3H), 1.67 – 1.52 (m, 4H), 1.46 – 1.30 (m, 3H), 1.24 (td, J = 13.5, 3.6 Hz, 2H), 1.04 (tt, J = 12.0, 3.3 Hz, 1H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, CD_3OD) δ 166.4, 166.1, 103.6, 85.4, 67.8, 35.8, 33.6, 33.2, 30.1, 28.0, 27.0, 23.4.

FTIR (NaCl, thin film, cm^{-1}): 2952, 2851, 2734, 1704, 1622, 1452, 1399, 1212, 1147, 979.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{18}H_{29}O_6^-$ $(M–Cs)^-$: 341.1970, found: 341.1974.

c. Preparation of cesium *trans*-2-((1-(2-(1,3-dioxan-2-yl)ethyl)-4-(*tert*-butyl)cyclohexyl)oxy)-2-oxoacetate (1c')



***trans*-1-(2-(1,3-dioxan-2-yl)ethyl)-4-(*tert*-butyl)cyclohexyl methyl oxalate (SI-7):** To a 50 mL round bottom flask containing a solution of alcohol **SI-5** (136 mg, 0.50 mmol) in CH_2Cl_2 (4.6 mL) at 0 °C was added Et_3N (0.11 mL, 0.75 mmol, 1.5 equiv), DMAP (6 mg, 0.05 mmol, 0.1 equiv), and methyl oxalyl chloride (0.06 mL, 0.60 mmol, 1.2 equiv) dropwise via syringe. The reaction was stirred at room temperature for 3 h followed by the addition of a 1:1 mixture of saturated aqueous NaCl and H_2O (2 mL). The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (4 x 4 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (10–20% EtOAc/hexanes) to furnish methyl oxalate **SI-7** (159 mg, 88% yield) as a clear colorless oil.

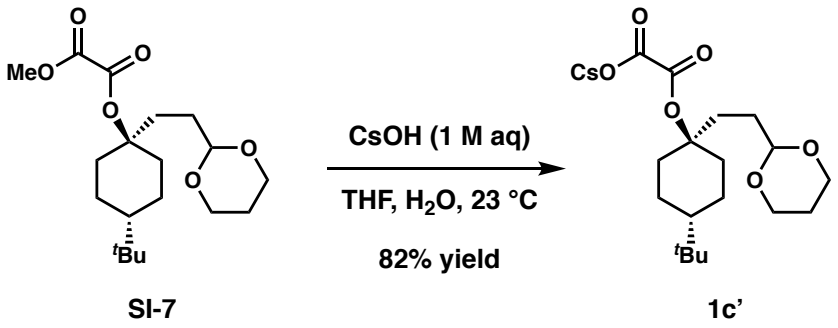
TLC R_f = 0.54 (40% EtOAc/hexanes, UV, $KMnO_4$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49 (t, *J* = 5.2 Hz, 1H), 4.07 (ddt, *J* = 10.4, 5.0, 1.4 Hz, 2H), 3.83 (s, 3H), 3.73 (dddd, *J* = 11.9, 10.4, 2.6, 1.6 Hz, 2H), 2.33 – 2.19 (m, 2H), 2.14 – 1.96 (m, 3H), 1.82 – 1.66 (m, 4H), 1.66 – 1.52 (m, 2H), 1.32 (dtt, *J* = 13.5, 2.7, 1.4 Hz, 1H), 1.26 – 1.02 (m, 3H), 0.83 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 156.6, 102.2, 90.0, 67.0, 53.4, 47.3, 34.6, 32.3, 28.8, 27.7, 26.4, 25.9, 24.1.

FTIR (NaCl, thin film, cm^{-1}): 2954, 2868, 2731, 2658, 1767, 1740, 1461, 1367, 1326, 1206, 1166, 1093, 1010, 973.

HRMS (FAB+, *m/z*): calc'd for $C_{19}H_{31}O_6$ $(M+H-H_2)^+$: 355.2121, found: 355.2133.



SI-7 **1c'**

cesium *trans*-2-((1-(2-(1,3-dioxan-2-yl)ethyl)-4-(*tert*-butyl)cyclohexyl)oxy)-2-oxoacetate (1c'): A 20 mL scintillation vial was charged with methyl oxalate **SI-7** (118 mg, 0.33 mmol), THF (2.1 mL), and H_2O (0.22 mL). A 1 M aqueous solution of CsOH (1 M in H_2O, 0.33 mL, 0.33 mmol, 1.0 equiv) was added dropwise to the solution with vigorous stirring. After the addition was complete, the mixture was stirred for an additional 5 min. The reaction was concentrated under reduced pressure to remove the THF and the aqueous layer was washed with 1:1 pentane/Et_2O (4 x 2 mL). The aqueous layer was concentrated under reduced pressure using rotary evaporation followed by high vacuum (~50 mTorr) to afford cesium oxalate **1c'** as a white solid (129 mg, 82% yield).

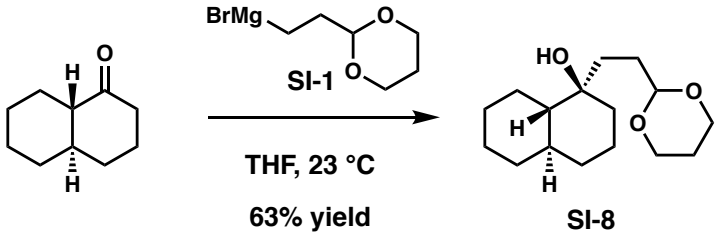
^{1}H NMR (400 MHz, CD_3OD) δ 4.56 (t, *J* = 5.2 Hz, 1H), 4.04 (ddt, *J* = 10.5, 5.1, 1.4 Hz, 2H), 3.78 (dddd, *J* = 12.0, 10.5, 2.6, 1.6 Hz, 2H), 2.36 – 2.26 (m, 2H), 2.15 – 2.07 (m, 2H), 2.00 (dtt, *J* = 13.4, 12.5, 5.0 Hz, 1H), 1.71 (td, *J* = 11.5, 5.9 Hz, 4H), 1.64 – 1.52 (m, 2H), 1.35 (dtt, *J* = 13.4, 2.6, 1.4 Hz, 1H), 1.24 – 1.06 (m, 3H), 0.88 (s, 9H).

^{13}C NMR (101 MHz, CD_3OD) δ 166.5, 165.9, 103.6, 87.2, 67.9, 35.9, 33.0, 29.8, 28.0, 27.2, 27.0, 25.0.

FTIR (NaCl, thin film, cm^{-1}): 2952, 2867, 2732, 2662, 1713, 1645, 1462, 1373, 1210, 1146, 1091, 1006, 972.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{18}H_{29}O_6^-$ $(M–Cs)^-$: 341.1970, found: 341.1972.

d. Preparation of cesium 2-(((1*R*,4a*R*,8a*S*)-1-(2-(1,3-dioxan-2-yl)ethyl)decahydronaphthalen-1-yl)oxy)-2-oxoacetate (1d)



(1*R*,4a*R*,8a*S*)-1-(2-(1,3-dioxan-2-yl)ethyl)decahydronaphthalen-1-ol (SI-8): A flame-dried 50 mL round bottom flask was charged with *trans*-decalone (500 mg, 3.28 mmol) and put under an atmosphere of nitrogen. THF (3.3 mL) was added, followed by dropwise addition of a solution of Grignard reagent **SI-1**[4] (8.2 mL, 1.25 mmol, 0.5 M in THF, 1.25 equiv) at 23 °C. TLC analysis indicated full conversion after 2 h, and the mixture was quenched with a saturated aqueous solution of NH_4Cl (5 mL) and stirred vigorously for 10 min. The biphasic mixture was concentrated under rotary evaporation to remove the THF. A saturated aqueous solution of NaCl (3 mL) was added and the resulting solution was extracted with EtOAc (4 x 15 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (0–40% EtOAc/hexanes) to provide tertiary alcohol **SI-8** (553 mg, 63% yield) as a white solid.

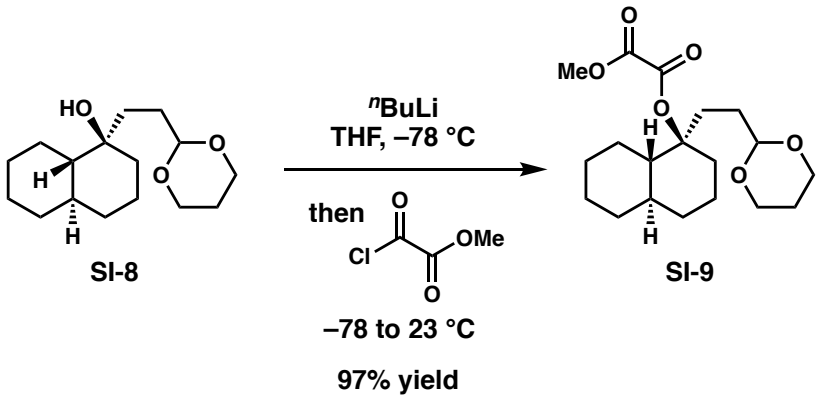
TLC R_f = 0.31 (33% EtOAc/hexanes, *p*-anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (t, *J* = 4.7 Hz, 1H), 4.09 (ddt, *J* = 10.4, 5.0, 1.4 Hz, 2H), 3.75 (td, *J* = 12.3, 2.5 Hz, 2H), 2.07 (dtt, *J* = 13.5, 12.4, 5.0 Hz, 1H), 1.81 – 1.71 (m, 2H), 1.60 (dddd, *J* = 19.4, 10.4, 4.6, 2.5 Hz, 7H), 1.55 – 1.46 (m, 3H), 1.39 – 1.25 (m, 3H), 1.19 (tdd, *J* = 8.8, 4.2, 2.5 Hz, 2H), 1.13 – 1.01 (m, 1H), 0.98 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 102.8, 72.4, 67.1, 49.0, 37.2, 36.7, 34.8, 34.6, 34.3, 29.7, 26.9, 26.3, 25.9, 24.9, 21.3.

FTIR (NaCl, thin film, cm^{-1}): 3495, 2925, 2849, 1448, 1377, 1145, 999.

HRMS (EI, *m/z*): calc'd for $C_{16}H_{28}O_3$ $(M+\cdot)^+$: 268.2039, found: 268.2054.



(1*R*,4a*R*,8a*S*)-1-(2-(1,3-dioxan-2-yl)ethyl)decahydronaphthalen-1-yl methyl oxalate (SI-9): A flame-dried 25 mL round bottom flask was charged with alcohol **SI-8** (240 mg, 0.89 mmol) and THF (3.6 mL). The flask was cooled to –78 ºC followed by dropwise addition of ^{n}BuLi (2.5 M in hexanes, 0.46 mL, 1.16 mmol, 1.3 equiv). The reaction was then stirred for an additional 30 min. Methyl oxalyl chloride (30 µL, 0.31 mmol, 1.7 equiv) was added dropwise by syringe. The solution was stirred at –78 ºC for 30 min and then warmed to room temperature over 2 h. The reaction was quenched with a 1:1 mixture of a saturated aqueous solution of $NaHCO_3$ and a saturated aqueous solution of NaCl (3 mL). The biphasic mixture was concentrated under rotary evaporation to remove the THF and the resulting solution was extracted with EtOAc (4 x 5 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (0–25% EtOAc/hexanes) to afford methyl oxalate **SI-9** (306 mg, 97% yield) as a viscous yellow oil.

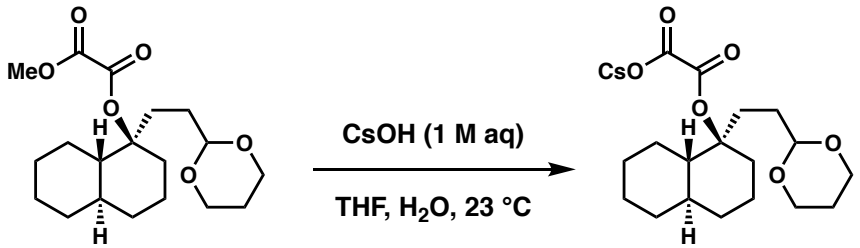
TLC R_f = 0.35 (15% EtOAc/hexanes, *p*-anisaldehyde).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.47 (t, *J* = 5.1 Hz, 1H), 4.12 – 4.04 (m, 2H), 3.86 (s, 3H), 3.73 (tdd, *J* = 12.0, 5.0, 2.6 Hz, 2H), 2.72 – 2.63 (m, 1H), 2.39 (ddd, *J* = 13.4, 11.3, 5.8 Hz, 1H), 2.06 (dtt, *J* = 13.5, 12.5, 5.0 Hz, 1H), 1.94 – 1.84 (m, 1H), 1.83 – 1.71 (m, 2H), 1.70 – 1.61 (m, 2H), 1.61 – 1.10 (m, 11H), 1.02 (ddd, *J* = 11.6, 10.4, 3.0 Hz, 1H), 0.99 – 0.86 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 156.8, 102.2, 91.2, 67.02, 66.99, 53.3, 47.8, 36.6, 34.6, 33.7, 31.9, 30.3, 29.4, 26.7, 26.1, 25.8, 24.7, 21.1.

FTIR (NaCl, thin film, cm^{-1}): 2931, 2851, 2732, 2662, 1766, 1739, 1450, 1330, 1205, 1170, 1144, 1002.

HRMS (FAB+, *m/z*): calc'd for $C_{19}H_{29}O_6$ $(M+H–H_2)^+$: 353.1964, found: 353.1969.



cesium 2-(((1*R*,4a*R*,8a*S*)-1-(2-(1,3-dioxan-2-yl)ethyl)decahydronaphthalen-1-yl)oxy)-2-oxoacetate (1d): A 20 mL scintillation vial was charged with methyl oxalate **SI-9** (141 mg, 0.40 mmol), THF (2.5 mL), and H_2O (0.26 mL). A 1 M aqueous solution of CsOH (1 M in H_2O, 0.40 mL, 0.40 mmol, 1.0 equiv) was added dropwise to the solution with vigorous stirring. After the addition was complete, the mixture was stirred for an additional 5 min. The reaction was then concentrated under reduced pressure to remove the THF and the aqueous layer was washed with 1:1 pentane/Et_2O (4 x 2 mL). The aqueous layer was concentrated under reduced pressure using rotary evaporation and then high vacuum (~50 mTorr) to deliver cesium oxalate **1d** as a hygroscopic white solid (177 mg, 94% yield).

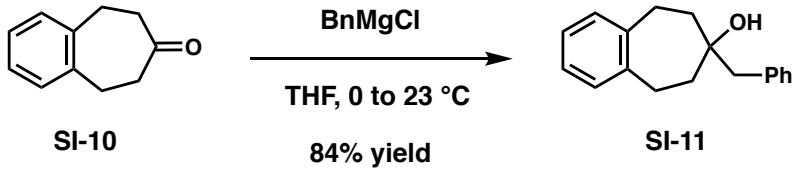
^{1}H NMR (400 MHz, CD_3OD) δ 4.51 (t, *J* = 5.1 Hz, 1H), 4.04 (ddt, *J* = 10.5, 5.0, 1.4 Hz, 2H), 3.78 (dddd, *J* = 14.6, 10.6, 3.5, 2.0 Hz, 2H), 2.76 – 2.63 (m, 1H), 2.51 – 2.32 (m, 1H), 1.99 (dtt, *J* = 13.4, 12.5, 5.0 Hz, 1H), 1.87 (ddd, *J* = 13.4, 10.2, 7.7 Hz, 1H), 1.82 – 1.70 (m, 2H), 1.69 – 1.14 (m, 13H), 1.09 – 0.87 (m, 3H).

^{13}C NMR (101 MHz, CD_3OD) δ 167.3, 166.8, 103.5, 88.6, 67.9, 37.5, 35.9, 35.1, 33.2, 31.2, 30.4, 27.7, 27.2, 27.0, 25.6, 22.1.

FTIR (NaCl, thin film, cm^{-1}): 2930, 2850, 2732, 2665, 1706, 1632, 1448, 1404, 1217, 1145, 1076, 1026, 1001.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{18}H_{27}O_6^-$ $(M–Cs)^-$: 339.1813, found: 339.1812.

e. Preparation of cesium 2-((7-benzyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-7-yl)oxy)-2-oxoacetate (1f)



7-benzyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-7-ol (SI-11): To a 50 mL round bottom flask containing a solution of cycloheptanone **SI-10** (100 mg, 0.62 mmol)[5] in THF (2.5 mL) at 0 °C was added a solution of benzylmagnesium chloride (2.0 M in THF, 0.47 mL, 0.94 mmol, 1.5 equiv) dropwise. The reaction was stirred at room temperature for 16 h and a saturated aqueous solution of NH_4Cl (2 mL) was slowly added. The biphasic mixture was concentrated under rotary evaporation to remove the THF. A saturated aqueous solution of NaCl (2 mL) was added and the resulting mixture was extracted with Et_2O (4 x 5 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (5–15% EtOAc/hexanes) to furnish tertiary alcohol **SI-11** (132 mg, 84% yield) as a white solid.

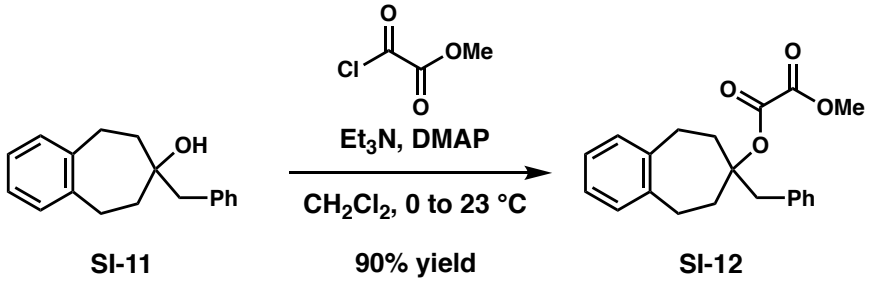
TLC R_f = 0.23 (10% EtOAc/hexanes, UV, $KMnO_4$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 3H), 7.21 – 7.15 (m, 2H), 7.09 (s, 4H), 3.16 (t, *J* = 13.3 Hz, 2H), 2.74 (s, 2H), 2.50 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.80 (dd, *J* = 14.0, 7.4 Hz, 2H), 1.58 (t, *J* = 13.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 136.9, 130.9, 128.8, 128.4, 126.7, 126.3, 73.6, 50.8, 39.1, 29.6.

FTIR (NaCl, thin film, cm^{-1}): 3557, 3455, 3060, 3026, 2931, 2853, 1493, 1454, 1223, 1086, 1042, 909.

HRMS (ESI, *m/z*): (EI, *m/z*): calc'd for $C_{18}H_{19}O$ $(M+H-H_2)^+$: 251.1436, found: 251.1433.



7-benzyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-7-yl methyl oxalate (SI-12): To a 50 mL round bottom flask containing a solution of alcohol **SI-11** (245 mg, 0.97 mmol) in CH_2Cl_2 (8.8

mL) at 0 °C was added Et_3N (0.2 mL, 1.46 mmol, 1.5 equiv), DMAP (12 mg, 0.10 mmol, 0.1 equiv), and methyl oxalyl chloride (0.11 mL, 1.17 mmol, 1.2 equiv) dropwise by syringe. The reaction was stirred at room temperature for 4.5 h followed by the addition of a 4:1 mixture of a saturated aqueous solution of NH_4Cl and a saturated aqueous solution of NaCl (5 mL). The organic layer was collected and the aqueous layer was extracted with Et_2O (4 x 8 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (5–10% EtOAc/hexanes) to afford methyl oxalate **SI-12** (297 mg, 90% yield) as a clear crystalline solid.

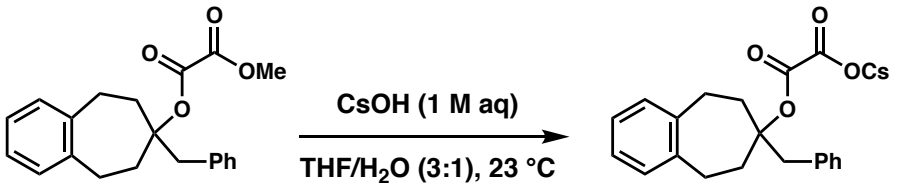
TLC R_f = 0.52 (15% EtOAc/hexanes, UV, $KMnO_4$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 4H), 7.15 – 7.10 (m, 2H), 7.08 (q, *J* = 1.2 Hz, 4H), 3.88 (s, 3H), 3.30 (s, 2H), 3.14 – 2.99 (m, 2H), 2.67 (dd, *J* = 14.2, 7.3 Hz, 2H), 2.56 (ddd, *J* = 14.9, 7.3, 1.3 Hz, 2H), 1.69 – 1.48 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 157.3, 142.1, 135.7, 130.7, 129.0, 128.4, 127.0, 126.5, 91.2, 53.5, 45.0, 35.9, 29.3.

FTIR (NaCl, thin film, cm^{-1}): 3028, 2952, 1766, 1738, 1494, 1454, 1326, 1202, 1165, 981.

HRMS (ESI, *m/z*): (EI, *m/z*): calc'd for $C_{21}H_{21}O_4$ $(M+H-H_2)^+$: 337.1440, found: 337.1435.



SI-12 **99% yield** **1f**

cesium 2-((7-benzyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-7-yl)oxy)-2-oxoacetate (1f): A 20 mL scintillation vial was charged with methyl oxalate **SI-12** (253 mg, 0.75 mmol), THF (4.7 mL), and H_2O (0.8 mL). A 1 M aqueous solution of CsOH (1 M in H_2O, 0.75 mL, 0.75 mmol, 1.0 equiv) was added dropwise to the solution with vigorous stirring. After the addition was complete, the mixture was stirred for an additional 5 min. The reaction was concentrated under reduced pressure using rotary evaporation and then high vacuum (~50 mTorr) to provide cesium oxalate **1f** as a white solid (339 mg, 99% yield).

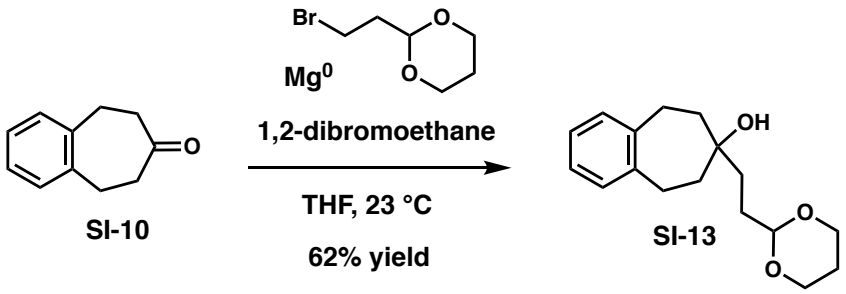
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.28 – 7.14 (m, 5H), 7.11 – 6.99 (m, 4H), 3.20 (s, 2H), 3.01 (t, *J* = 12.9 Hz, 2H), 2.48 – 2.36 (m, 4H), 1.32 (t, *J* = 13.1 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.9, 163.3, 142.4, 136.9, 130.7, 128.5, 127.8, 126.2, 126.0, 83.7, 44.1, 35.8, 28.4.

IR (ATR, cm^{-1}): 3374, 2965, 1712, 1627, 1396, 1208, 1185.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{20}H_{19}O_4$ $(M-Cs)^-$: 323.1289, found: 323.1292.

f. Preparation of cesium 2-((7-(2-(1,3-dioxan-2-yl)ethyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-7-yl)oxy)-2-oxoacetate (1g)



7-(2-(1,3-dioxan-2-yl)ethyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-7-ol (SI-13):

A flame-dried 25 mL round bottom flask was charged with magnesium turnings (99 mg, 4.06 mmol, 2.6 equiv). The vessel was exchanged three times with argon and THF (1.0 mL) was added. With vigorous stirring, 1,2-dibromoethane (35 µL, 0.41 mmol, 0.26 equiv) was added dropwise to the suspension. After 10 min, a solution of 2-(2-bromoethyl)-1,3-dioxane (517 mg, 2.65 mmol, 1.7 equiv) in THF (2.0 mL) was added dropwise over 10 min. Upon completion of addition, the reaction was stirred for an additional 1.5 h, yielding a grey solution. A separate flame-dried 50 mL round bottom flask was charged with cyclopentanone **SI-10** (250 mg, 1.56 mmol)[5] and THF (2.0 mL) to which the Grignard reagent was added dropwise via syringe. The Grignard reagent flask was rinsed with THF (1.0 mL) and added to the reaction for quantitative transfer. The resulting solution was stirred for 22 h and then quenched with the addition of a saturated aqueous solution of NH_4Cl (3 mL) and stirred vigorously for 10 min. The biphasic mixture was concentrated under rotary evaporation to remove the THF. A saturated aqueous solution of NaCl (2 mL) was added and the resulting solution was extracted with Et_2O (4 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (10–50% EtOAc/hexanes) to give tertiary alcohol **SI-13** (267 mg, 62% yield) as a clear crystalline solid.

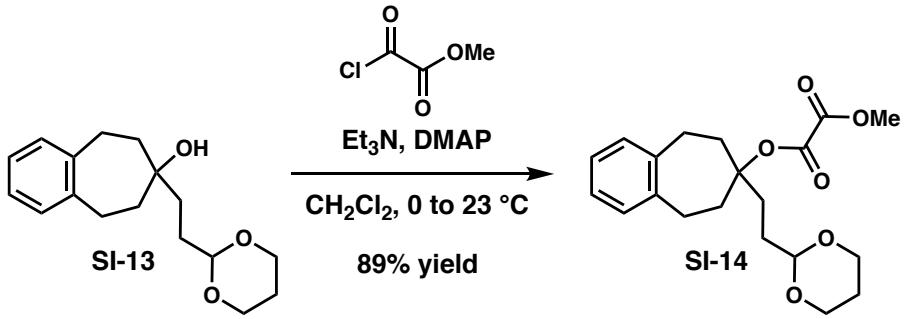
TLC R_f = 0.34 (50% EtOAc/hexanes, UV, $KMnO_4$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 4H), 4.57 (t, *J* = 4.8 Hz, 1H), 4.12 (ddt, *J* = 10.5, 5.0, 1.4 Hz, 2H), 3.83 – 3.66 (m, 2H), 3.18 (t, *J* = 13.2 Hz, 2H), 2.52 (ddd, *J* = 14.6, 7.7, 1.4 Hz, 2H), 2.32 (t, *J* = 11.3 Hz, 1H), 2.18 – 2.00 (m, 1H), 1.84 (dd, *J* = 13.9, 7.8 Hz, 2H), 1.75 (dtd, *J* = 10.6, 5.1, 2.8 Hz, 2H), 1.61 (dd, *J* = 8.9, 6.4 Hz, 2H), 1.51 (t, *J* = 12.9 Hz, 2H), 1.35 (dtt, *J* = 13.5, 2.6, 1.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 128.8, 126.1, 102.6, 72.9, 67.0, 39.2, 38.0, 29.7, 29.0, 25.8.

FTIR (NaCl, thin film, cm^{-1}): 3457, 2932, 2853, 1492, 1454, 1404, 1144, 1097, 1014, 998, 903.

HRMS (EI, *m/z*): calc'd for $C_{17}H_{23}O_3$ $(M+H-H_2)^+$: 275.1647, found: 275.1638.



7-(2-(1,3-dioxan-2-yl)ethyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-7-yl methyl oxalate (SI-14): To a 50 mL round bottom flask containing a solution of alcohol **SI-13** (202 mg, 0.73 mmol) in CH_2Cl_2 (6.6 mL) at 0 °C was added Et_3N (0.15 mL, 1.09 mmol, 1.5 equiv), DMAP (9 mg, 0.07 mmol, 0.1 equiv), and methyl oxalyl chloride (0.11 mL, 1.17 mmol, 1.2 equiv) dropwise by syringe. The reaction was stirred at room temperature for 3 h followed by the addition of a 3:1 mixture of a saturated aqueous solution of NH_4Cl and a saturated aqueous solution of NaCl (4 mL). The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (3 x 6 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (10–33% EtOAc/hexanes) to afford methyl oxalate **SI-14** (237 mg, 89% yield) as a white crystalline solid.

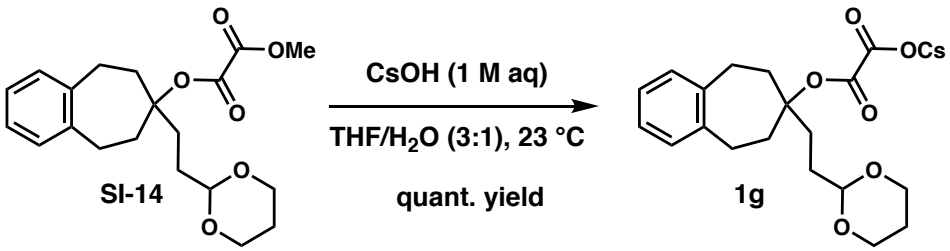
TLC R_f = 0.34 (33% EtOAc/hexanes, UV, $KMnO_4$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 4H), 4.48 (t, *J* = 5.1 Hz, 1H), 4.07 (ddt, *J* = 10.4, 5.0, 1.4 Hz, 2H), 3.88 (s, 3H), 3.72 (dddd, *J* = 11.9, 10.5, 2.6, 1.6 Hz, 2H), 3.15 – 2.95 (m, 2H), 2.59 (ddt, *J* = 14.0, 10.5, 6.6 Hz, 4H), 2.15 – 1.94 (m, 3H), 1.72 – 1.43 (m, 4H), 1.32 (dtt, *J* = 13.4, 2.6, 1.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 156.6, 142.1, 129.0, 126.5, 102.0, 91.2, 67.0, 53.5, 36.0, 32.9, 29.4, 29.2, 25.8.

FTIR (NaCl, thin film, cm^{-1}): 2954, 2852, 2732, 1765, 1740, 1494, 1454, 1327, 1206, 1168, 1085, 1009, 894.

HRMS (EI, *m/z*): calc'd for $C_{20}H_{25}O_6$ $(M+H-H_2)^+$: 361.1651, found: 361.1652.



cesium 2-((7-(2-(1,3-dioxan-2-yl)ethyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-7-yl)oxy)-2-oxoacetate (1g): A 20 mL scintillation vial was charged with methyl oxalate **SI-14** (180 mg, 0.50

mmol), THF (3.1 mL), and H_2O (0.53 mL). A 1 M aqueous solution of CsOH (1 M in H_2O, 0.5 mL, 0.50 mmol, 1.0 equiv) was added dropwise to the solution with vigorous stirring. After the addition was complete, the mixture was stirred for an additional 5 min. The reaction was concentrated under reduced pressure using rotary evaporation and then high vacuum (~50 mTorr) to give cesium oxalate **1g** as a hygroscopic white solid (242 mg, quant. yield).

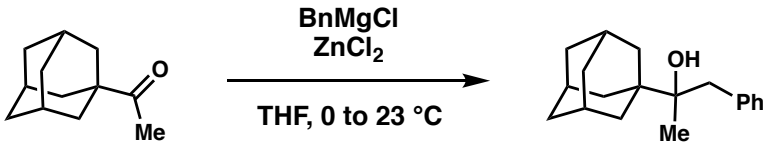
^{1}H NMR (400 MHz, D_2O) δ 7.24 – 7.01 (m, 4H), 4.66 (t, *J* = 5.3 Hz, 1H), 4.05 (ddd, *J* = 12.2, 5.0, 1.3 Hz, 2H), 3.83 (td, *J* = 12.4, 2.4 Hz, 2H), 2.98 (dd, *J* = 14.6, 11.6 Hz, 2H), 2.56 (dd, *J* = 14.7, 7.7 Hz, 2H), 2.47 (dd, *J* = 14.5, 7.7 Hz, 2H), 2.10 – 1.82 (m, 3H), 1.72 – 1.34 (m, 5H).

^{13}C NMR (101 MHz, D_2O) δ 167.5, 166.5, 145.2, 131.4, 129.1, 104.6, 91.9, 69.5, 38.0, 34.6, 31.1, 30.9, 27.6.

IR (ATR, cm^{-1}): 3399, 2933, 2856, 1711, 1638, 1375, 1206, 1145.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{19}H_{23}O_6$ $(M–Cs)^-$: 347.1500, found: 347.1503.

g. Preparation of cesium 2-((2-((3*r*,5*r*,7*r*)-adamantan-1-yl)-1-phenylpropan-2-yl)oxy)-2-oxoacetate (1h)



SI-15

2-((3*r*,5*r*,7*r*)-adamantan-1-yl)-1-phenylpropan-2-ol (SI-15): A flame-dried 25 mL round bottom flask was charged with $ZnCl_2$ (38 mg, 0.28 mmol, 0.25 equiv) and THF (1.7 mL). A solution of BnMgCl (2.0 M in THF, 1.1 mL, 02.24 mmol, 2.0 equiv) was added dropwise and the reaction was stirred for 1 h. The contents were then cooled to 0 ºC and a solution of 1-adamantyl methyl ketone (200 mg, 1.12 mmol) in THF (2.0 mL) was added dropwise. The reaction was stirred for 2 h at 0 ºC then warmed to room temperature over 12 h. A 4:1 mixture of a saturated aqueous solution of NH_4Cl and H_2O (2.5 mL) was slowly added and the biphasic mixture was concentrated under rotary evaporation to remove the THF. The resulting solution was extracted with Et_2O (4 x 4 mL). The combined organic extracts were washed with saturated aqueous NaCl (3 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude ratio of benzyl adduct **SI-15** to 1-adamantyl methyl ketone starting material was ~8:1. The crude residue was purified by silica gel chromatography (5–10% Et_2O/hexanes) to afford tertiary alcohol **SI-15** (247 mg, 82% yield) as a white solid.

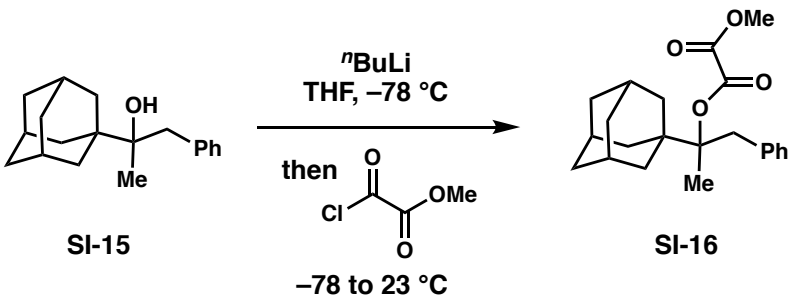
TLC R_f = 0.36 (15% Et_2O/hexanes, UV, $KMnO_4$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.15 (m, 5H), 2.92 (d, *J* = 13.1 Hz, 1H), 2.56 (d, *J* = 13.1 Hz, 1H), 2.13 – 1.94 (m, 3H), 1.76 (d, *J* = 3.1 Hz, 7H), 1.69 (ddt, *J* = 13.3, 9.4, 2.2 Hz, 5H), 1.13 – 1.03 (br s, 1H), 0.92 (d, *J* = 0.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 131.2, 128.1, 126.2, 75.8, 41.1, 39.3, 37.3, 36.4, 28.9, 20.8.

FTIR (NaCl, thin film, cm^{-1}): 3496, 2905, 2850, 1679, 1492, 1453, 1379, 1345, 1191, 1090, 927.

HRMS (EI, *m/z*): calc'd for $C_{19}H_{25}O$ $(M+H–H_2)^+$: 269.1905, found: 269.1900.



2-((3*r*,5*r*,7*r*)-adamantan-1-yl)-1-phenylpropan-2-yl methyl oxalate (SI-16): A flame-dried 25 mL round bottom flask was charged with alcohol **SI-15** (50 mg, 0.19 mmol) and THF (0.74 mL). The flask was cooled to –78 ºC followed by dropwise addition of ^{n}BuLi (2.05 M in hexanes, 0.11 mL, 0.22 mmol, 1.2 equiv). The reaction was stirred for an additional 30 min at the same temperature. Methyl oxalyl chloride (30 μL, 0.31 mmol, 1.7 equiv) was added dropwise via syringe. The reaction was stirred at –78 ºC for 1 h and then warmed to room temperature over 3 h. The reaction was diluted with Et_2O (1.5 mL) and quenched with a 1:1 mixture of a saturated aqueous solution of $NaHCO_3$ and a saturated aqueous solution of NaCl (2 mL). The biphasic mixture was concentrated under rotary evaporation to remove the THF and the resulting solution was extracted with Et_2O (4 x 3 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (5–15% Et_2O/hexanes) to provide methyl oxalate **SI-16** (51 mg, 77% yield) as a white crystalline solid.

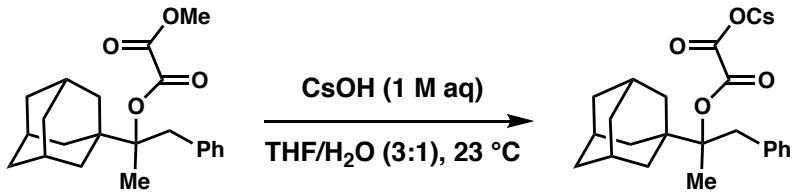
TLC R_f = 0.40 (10% EtOAc/hexanes, UV, $KMnO_4$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.05 (m, 5H), 3.89 (s, 3H), 3.33 (d, *J* = 13.6 Hz, 1H), 2.73 (dd, *J* = 13.9, 2.6 Hz, 1H), 2.15 – 1.97 (m, 3H), 1.92 – 1.80 (m, 3H), 1.71 (p, *J* = 12.7, 12.2 Hz, 9H), 1.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 156.9, 137.4, 131.1, 128.1, 126.6, 96.0, 53.4, 41.4, 40.9, 37.0, 36.9, 28.6, 18.6.

FTIR (NaCl, thin film, cm^{-1}): 3028, 2906, 2850, 1766, 1744, 1604, 1496, 1454, 1323, 1208, 1158, 984.

HRMS (EI, *m/z*): calc'd for $C_{22}H_{27}O_4$ $(M+H–H_2)^+$: 355.1909, found: 355.1921.



SI-16 **1h**

cesium 2-((2-((3*r*,5*r*,7*r*)-adamantan-1-yl)-1-phenylpropan-2-yl)oxy)-2-oxoacetate (1h): A 20 mL scintillation vial was charged with methyl oxalate **SI-16** (292 mg, 0.82 mmol), THF (5.1 mL), and H_2O (0.88 mL). A 1 M aqueous solution of CsOH (0.82 mL, 0.82 mmol, 1.0 equiv) was then added dropwise with vigorous stirring. After the addition was complete, the mixture was stirred for an additional 5 min. The vial was then concentrated under reduced pressure using rotary evaporation followed by high vacuum (~50 mTorr) to afford cesium oxalate **1h** as a white solid (391 mg, quant. yield).

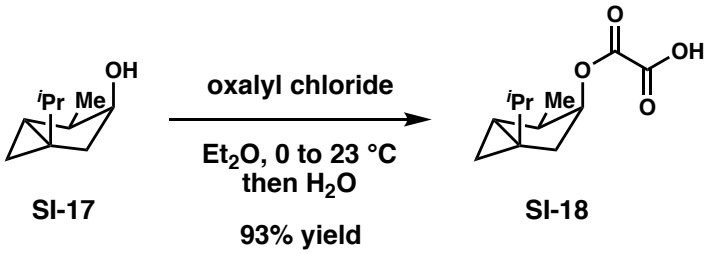
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.39 – 7.26 (m, 2H), 7.26 – 7.08 (m, 3H), 3.16 (d, J = 13.8 Hz, 1H), 2.79 (d, J = 13.9 Hz, 1H), 2.03 – 1.88 (m, 3H), 1.82 – 1.70 (m, 3H), 1.71 – 1.49 (m, 9H), 1.22 (s, 3H).

^{13}C NMR (101 MHz, DMSO- d_6) δ 167.8, 163.7, 138.8, 130.8, 127.7, 125.8, 88.3, 40.7, 36.6, 36.1, 28.1, 19.4.

IR (ATR, cm^{-1}): 3398, 2902, 2846, 1711, 1616, 1453, 1239, 1086, 893.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{21}H_{25}O_4$ $(M–Cs)^–$: 341.1758, found: 341.1763.

h. Preparation of cesium 2-(((1*S*,3*S*,4*R*,5*R*)-1-isopropyl-4-methylbicyclo[3.1.0]hexan-3-yl)oxy)-2-oxoacetate (1k)



SI-17 SI-18

2-(((1*S*,3*S*,4*R*,5*R*)-1-isopropyl-4-methylbicyclo[3.1.0]hexan-3-yl)oxy)-2-oxoacetic acid (SI-18): A flame-dried 25 mL round bottom flask was charged with Et_2O (5 mL) and cooled to 0 °C. Oxalyl chloride (165 µL, 2.05 mmol, 2.05 equiv) was added. In a separate, flame-dried 2 dram vial, (–)-Thujol **SI-17** (158 mg, 1.02 mmol)[6] was dissolved in Et_2O (2 mL). The alcohol was added dropwise to the oxalyl chloride solution at 0 °C, and the vial containing the alcohol was rinsed with Et_2O (1 mL), which was then also added dropwise to the reaction flask. The mixture was stirred for 2 h at 0 °C and 1 h at 23 °C. Oxalyl chloride (40 µL, 0.51 mmol, 0.5 equiv) was then added at 23 °C, and the reaction was stirred for an additional 2 h, until all alcohol had been consumed by TLC analysis. The mixture was concentrated under reduced pressure and dried under high vacuum (~90 mTorr) for 10 min. The residue was subsequently taken up in Et_2O (20 mL), and H_2O (20 mL) was added carefully, dropwise. The mixture was stirred vigorously until bubbling ceased (10 min), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 10 mL), and the combined organic layers were extracted with saturated aqueous $NaHCO_3$ (2 x 25 mL). The combined bicarbonate layers were washed with Et_2O (1 x 20 mL), and were subsequently acidified with 1 M HCl (35 mL), which was slowly added in portions of 5 mL to give a pH of 3. The resulting acidified aqueous layer was extracted with Et_2O (4 x 20 mL), and the combined organic layers washed with a saturated aqueous solution of NaCl (1 x 40 mL), dried with Na_2SO_4, filtered, and concentrated under reduced pressure to afford **SI-18** as a clear oil (216 mg, 93% yield). *Note:* this oil will slowly decompose, even under high vacuum, if left for extended periods of time (> 6 h). This decomposition was noted with slight color change to purple. The oil should be dried and carried forward as quickly as possible.

$[\alpha]_D^{25}$ = –38.2° (c = 0.18, $CHCl_3$).

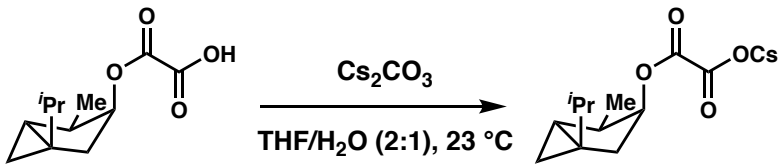
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 1H), 4.87 (dt, *J* = 9.0, 7.3 Hz, 1H), 2.49 (p, *J* = 7.0 Hz, 1H), 2.10 (dd, *J* = 12.4, 7.6 Hz, 1H), 1.96 – 1.85 (m, 1H), 1.30 (dt, *J* = 13.7, 6.8 Hz, 1H), 0.98 (d,

J = 6.7 Hz, 3H), 1.00 – 0.88 (m, 1H), 0.94 (d, J = 5.1 Hz, 3H), 0.92 (d, J = 5.0 Hz, 3H), 0.42 – 0.30 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 157.7, 79.8, 35.9, 33.1, 31.1, 30.0, 27.9, 20.2, 19.7, 15.3, 14.6.

FTIR (NaCl, thin film, cm^{-1}): 3178, 2960, 2874, 1744, 1203, 979.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{12}H_{17}O_4$ $(M–H)^–$: 225.1127, found: 225.1122.



SI-18 **quant. yield** **1k**

cesium 2-(((1*S*,3*S*,4*R*,5*R*)-1-isopropyl-4-methylbicyclo[3.1.0]hexan-3-yl)oxy)-2-oxoacetate (1k): A 20 mL scintillation vial was charged with oxalic acid **SI-18** (211 mg, 0.93 mmol) and THF (3.1 mL). Cs_2CO_3 (152 mg, 0.47 mmol, 0.5 equiv) was taken up in H_2O (1.05 mL) in a separate vial, and transferred to the vigorously stirred acid at room temperature. The vial containing the base was rinsed with H_2O (0.5 mL) and transferred dropwise to the reaction. After stirring vigorously at room temperature for 5 min, the mixture was concentrated under reduced pressure and azeotroped with PhMe (6 x 5 mL) to afford **1k** as a white solid (333 mg, quant. yield).

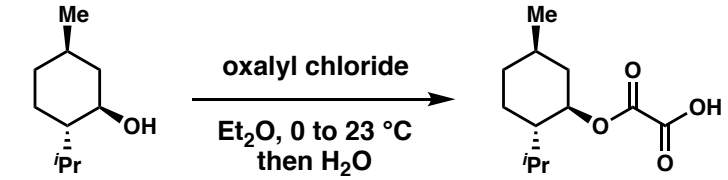
^{1}H NMR (400 MHz, DMSO-d_6) δ 4.54 (dt, J = 9.3, 7.3 Hz, 1H), 2.26 (p, J = 6.9 Hz, 1H), 1.86 (dd, J = 12.2, 7.7 Hz, 1H), 1.65 (ddd, J = 12.2, 9.4, 1.4 Hz, 1H), 1.27 (hept, J = 6.7 Hz, 1H), 0.93 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.9 Hz, 3H), 0.91 – 0.82 (m, 1H), 0.78 (d, J = 7.0 Hz, 3H), 0.39 (dd, J = 5.1, 3.9 Hz, 1H), 0.25 (ddd, J = 8.3, 5.1, 1.4 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.2, 162.8, 72.6, 35.1, 32.4, 30.3, 29.6, 27.5, 20.1, 19.5, 15.1, 13.8.

IR (ATR, cm^{-1}): 3408, 2957, 1718, 1633, 1375, 1202, 1037.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{12}H_{17}O_4$ $(M–Cs)^–$: 225.1127, found: 225.1135.

i. Preparation of cesium 2-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)-2-oxoacetate (1m)



(–)-menthol quant. yield SI-19

2-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)-2-oxoacetic acid (SI-19): A flame-dried 100 mL round bottom flask was charged with (–)-menthol (400 mg, 2.56 mmol) and Et_2O (20 mL). The flask was cooled to 0 °C, and oxalyl chloride (0.41 mL, 5.12 mmol, 2.0 equiv) was added dropwise. The mixture was warmed to room temperature after 10 min, and after an additional 1.5 h, TLC analysis indicated consumption of (–)-menthol. The reaction was carefully quenched at 0 °C by the dropwise addition of H_2O (30 mL) after addition of a vent needle. The mixture was stirred vigorously and warmed to room temperature. The layers were separated, and the aqueous layer extracted with Et_2O (3 x 15 mL), and the combined organic layers dried with $MgSO_4$, filtered, and concentrated under reduced pressure and azeotroped with pentane (4 x 20 mL) to afford **SI-19** as a clear oil (584 mg, quant. yield).

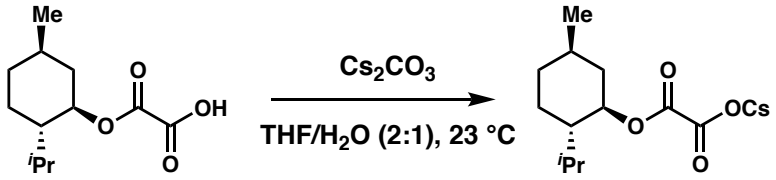
$[\alpha]_D^{25}$ = –80.8° (c = 0.89, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (bs, 1H), 4.87 (td, *J* = 11.0, 4.5 Hz, 1H), 2.05 (dddd, *J* = 11.9, 4.4, 3.4, 1.9 Hz, 1H), 1.88 (heptd, *J* = 6.9, 2.7 Hz, 1H), 1.78 – 1.67 (m, 2H), 1.63 – 1.45 (m, 2H), 1.18 (td, *J* = 12.0, 11.0 Hz, 1H), 1.13 – 1.01 (m, 1H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.99 – 0.84 (m, 1H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.77 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 157.5, 79.7, 46.7, 40.3, 34.0, 31.6, 26.3, 23.4, 22.0, 20.7, 16.3.

FTIR (NaCl, thin film, cm^{-1}): 3180, 2957, 2872, 1739, 1456, 1202, 950.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{12}H_{19}O_4$ $(M-H)^-$: 227.1289, found: 227.1283.



SI-19 **quant. yield** **1m**

cesium 2-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)-2-oxoacetate (1m): Oxalic acid **SI-19** (566 mg, 2.48 mmol) was taken up in THF (8.3 mL). Cs_2CO_3 (404 mg, 1.24 mmol, 0.5 equiv) was taken up in H_2O (3.1 mL) in a vial, and transferred dropwise to the vigorously stirred acid at room temperature. The vial containing the base was rinsed with H_2O (1 mL) and transferred dropwise to the reaction. After stirring vigorously at room temperature for 10 min, the mixture was concentrated under reduced pressure and azeotroped with PhMe (6 x 20 mL) to afford **1m** as a white solid (889 mg, quant. yield). This resulting cesium oxalate is moderately hygroscopic, and was generally stored and weighed out in a nitrogen-filled glovebox.

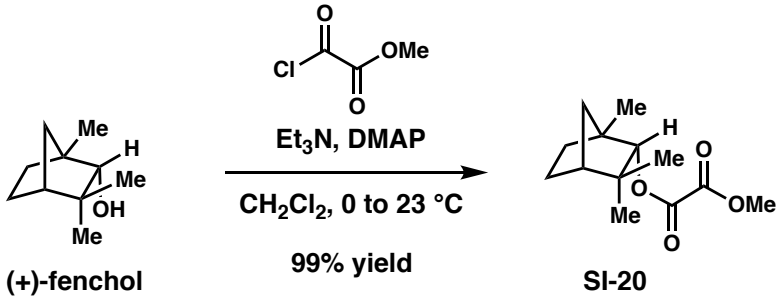
^{1}H NMR (400 MHz, D_2O) δ 4.75 (td, *J* = 11.0, 4.5 Hz, 1H), 1.94 (dtd, *J* = 13.0, 3.9, 1.9 Hz, 1H), 1.80 (heptd, *J* = 7.0, 2.6 Hz, 1H), 1.68 (ddt, *J* = 12.6, 9.1, 3.0 Hz, 2H), 1.55 – 1.40 (m, 2H), 1.17 – 1.01 (m, 2H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.96 – 0.81 (m, 1H), 0.87 (d, *J* = 7.1 Hz, 3zH), 0.73 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, D_2O) δ 167.3, 167.2, 80.0, 49.1, 42.6, 36.3, 33.7, 28.6, 25.8, 24.0, 22.5, 18.4.

IR (ATR, cm^{-1}): 2954, 1708, 1645, 1370, 1196, 963.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{12}H_{19}O_4$ $(M–Cs)^–$: 227.1289, found: 227.1280.

j. Preparation of cesium 2-oxo-2-(((1*S*,2*S*,4*R*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)acetate (1n)



methyl ((1*S*,2*S*,4*R*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl) oxalate (SI-20): To a 100 mL round bottom flask containing a solution of (+)-fenchol (400 mg, 2.59 mmol) in CH_2Cl_2 (24 mL) at 0 °C was added Et_3N (0.54 mL, 3.89 mmol, 1.5 equiv), DMAP (32 mg, 0.26 mmol, 0.1 equiv), and methyl oxalyl chloride (0.29 mL, 3.11 mmol, 1.2 equiv) dropwise via syringe. The reaction was stirred at room temperature for 3 h followed by the addition of a 3:1 mixture of a saturated aqueous solution of NH_4Cl and a saturated aqueous solution of NaCl (8 mL). The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (5–10% Et_2O/hexanes) to furnish methyl oxalate **SI-20** (617 mg, 99% yield) as a transparent crystalline solid.

TLC R_f = 0.63 (20% EtOAc/hexanes, UV, $KMnO_4$).

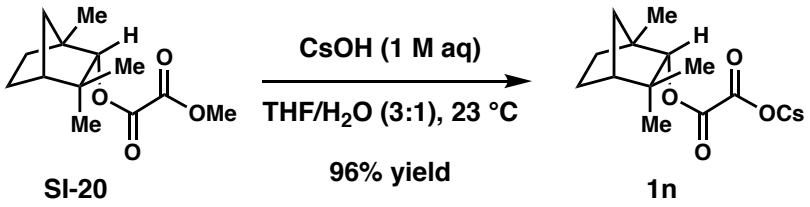
$[\alpha]_D^{25}$ = +48.8° (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (d, *J* = 2.0 Hz, 1H), 3.89 (s, 3H), 1.89 – 1.66 (m, 4H), 1.66 – 1.56 (m, 1H), 1.47 (tdd, *J* = 12.6, 5.7, 4.0 Hz, 1H), 1.23 (dd, *J* = 10.4, 1.6 Hz, 1H), 1.19 – 1.08 (m, 1H), 1.12 (s, 3H), 1.07 (s, 3H), 0.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 158.4, 89.6, 53.5, 48.6, 48.4, 41.5, 39.9, 29.8, 26.6, 25.9, 20.2, 19.4.

FTIR (NaCl, thin film, cm^{-1}): 2960, 2877, 1770, 1747, 1462, 1369, 1322, 1202, 1170, 1030, 968.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{13}H_{20}O_4Na$ $(M+Na)^+$: 263.1254, found: 263.1259.



cesium 2-oxo-2-(((1*S*,2*S*,4*R*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)acetate (1n): A 20 mL scintillation vial was charged with methyl oxalate **SI-20** (755 mg, 3.14 mmol), THF (9.8 mL), and H_2O (0.17 mL). A 1 M aqueous solution of CsOH (3.14 mL, 3.14 mmol, 1.0 equiv) was added

dropwise to the solution with vigorous stirring. After the addition was complete, the mixture was stirred for an additional 5 min. The reaction was concentrated under rotary evaporation to remove the THF. The aqueous layer was washed with Et_2O (3 x 2.5 mL) and then concentrated under reduced pressure using rotary evaporation followed by high vacuum (~50 mTorr) to afford cesium oxalate **1n** as a white solid (1.078 g, 96% yield).

$[\alpha]_D^{25}$ = +25.1° (c = 0.98, MeOH).

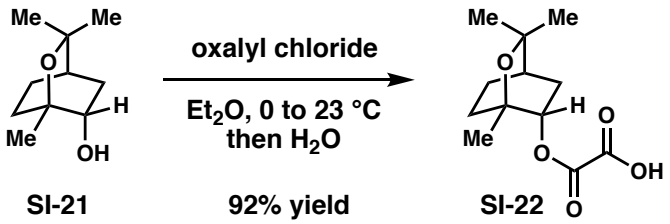
^{1}H NMR (400 MHz, DMSO-d_6) δ 4.17 (d, *J* = 1.9 Hz, 1H), 1.76 – 1.51 (m, 4H), 1.40 (tdd, *J* = 12.3, 5.6, 4.0 Hz, 1H), 1.14 (dd, *J* = 10.0, 1.6 Hz, 1H), 1.06 – 1.01 (m, 1H), 1.03 (s, 3H), 0.99 (s, 3H), 0.71 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 168.2, 163.1, 83.6, 47.80, 47.78, 40.9, 29.5, 26.2, 25.5, 20.1, 19.4.

IR (ATR, cm^{-1}): 3413, 2940, 2874, 1710, 1640, 1364, 1203, 1032, 1003.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{12}H_{17}O_4$ $(M–Cs)^-$: 225.1132, found: 225.1128.

k. Preparation of cesium 2-oxo-2-(((1*S*,4*R*,6*S*)-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-6-yl)oxy)acetate (1o)



SI-21 92% yield SI-22

2-oxo-2-(((1*S*,4*R*,6*S*)-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-6-yl)oxy)acetic acid (SI-22): A flame-dried 100 mL round bottom flask was charged with eucalyptol derivative **SI-21** (400 mg, 2.35 mmol)[7] and Et_2O (18 mL). The flask was cooled to 0 ºC, and oxalyl chloride (0.38 mL, 4.70 mmol, 2.0 equiv) was added dropwise. The clear mixture was stirred for 1.5 h, and then warmed to room temperature. After stirring for 24 h, the solution was cooled to 0 °C, and oxalyl chloride (0.1 mL, 1.18 mmol, 0.5 equiv) was added. The mixture was warmed to room temperature and stirred for an additional 4 h, until all alcohol had been consumed by TLC analysis. The mixture was concentrated under reduced pressure and dried under high vacuum (~90 mTorr) for 5 min. The residue was subsequently taken up in Et_2O (30 mL) and H_2O (30 mL) was added carefully, dropwise. The mixture was stirred vigorously until bubbling ceased (10 min), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 15 mL), and the combined organic layers were extracted with saturated aqueous $NaHCO_3$ (3 x 30 mL). The combined bicarbonate layers were acidified with 1 M HCl (110 mL), which was slowly added in portions of 10 mL to give a pH of 1. The resulting acidified aqueous layer was extracted with Et_2O (3 x 80 mL), and the combined organic layers washed with a saturated aqueous solution of NaCl (1 x 60 mL), dried with Na_2SO_4, filtered, and concentrated under reduced pressure to afford **SI-22** as a white solid (522 mg, 92% yield) after azeotroping with pentane.

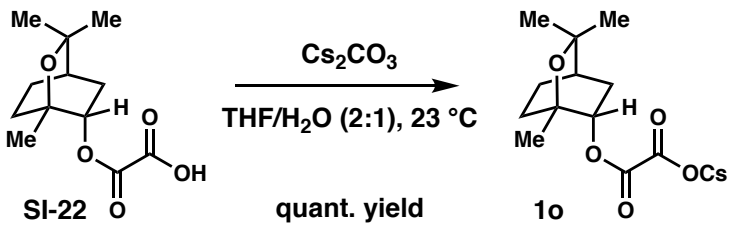
$[\alpha]_D^{25}$ = –9.5° (c = 0.53, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 4.88 (ddd, *J* = 9.8, 3.7, 2.0 Hz, 1H), 2.69 (ddt, *J* = 14.7, 9.7, 3.3 Hz, 1H), 2.09 – 2.01 (m, 1H), 1.97 (ddd, *J* = 14.7, 11.6, 2.9 Hz, 1H), 1.74 – 1.64 (m, 1H), 1.64 – 1.53 (m, 2H), 1.43 (ddd, *J* = 14.6, 3.6, 2.4 Hz, 1H), 1.33 (s, 3H), 1.26 (s, 3H), 1.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 158.0, 76.3, 75.1, 71.6, 33.9, 32.1, 28.7, 28.4, 25.7, 23.9, 21.8.

FTIR (NaCl, thin film, cm^{-1}): 3078, 2975, 1745, 1184, 1004.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{12}H_{17}O_5$ $(M–H)^–$: 241.1081, found: 241.1083.



cesium 2-oxo-2-(((1*S*,4*R*,6*S*)-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-6-yl)oxy)acetate (1o): A 20 mL scintillation vial was charged with oxalic acid **SI-22** (507 mg, 2.09 mmol) and THF (7 mL). Cs_2CO_3 (340.7 g, 1.05 mmol, 0.5 equiv) was taken up in H_2O (2.5 mL) in a separate vial, and transferred to the vigorously stirred acid at room temperature. The vial containing the base was rinsed with H_2O (1 mL) and transferred dropwise to the reaction. After stirring vigorously at room temperature for 5 min, the mixture was concentrated under reduced pressure and azeotroped with PhMe (8 x 6 mL) to afford **1o** as a white solid (780 mg, quant. yield). This resulting cesium oxalate is moderately hygroscopic, and was generally stored and weighed out in a nitrogen-filled glovebox.

^{1}H NMR (400 MHz, D_2O) δ 4.75 (ddd, *J* = 9.7, 3.6, 1.4 Hz, 1H), 2.63 (ddt, *J* = 13.1, 9.8, 3.2 Hz, 1H), 2.08 – 1.87 (m, 2H), 1.70 – 1.52 (m, 3H), 1.44 (dt, *J* = 14.7, 3.2 Hz, 1H), 1.30 (s, 3H), 1.23 (s, 3H), 1.05 (s, 3H).

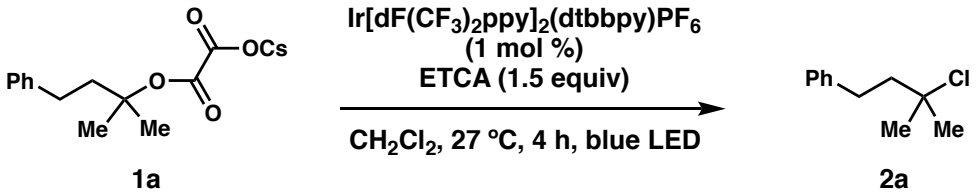
^{13}C NMR (101 MHz, D_2O) δ 167.1, 167.0, 78.5, 77.1, 74.7, 35.9, 33.9, 30.6, 30.2, 27.9, 25.8, 23.5.

IR (ATR, cm^{-1}): 2969, 1714, 1634, 1377, 1196, 1005, 874.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{12}H_{17}O_5$ $(M–Cs)^–$: 241.1081, found: 241.1090.

3. Deoxychlorination Reactions

Optimization of Reaction Parameters



1a **2a**

Entry[a]	Deviation from standard conditions	NMR yield **2a** (%)[b]
1	None	82
2	ETCA (not distilled)	32
3	HCA instead of ETCA	17
4	**A** instead of ETCA	0
5	**B** instead of ETCA	5
6	**C** instead of ETCA	75
7	NCS instead of ETCA	32
8	CCl_4 (10 equiv) instead of ETCA	42
9	MeCN instead of CH_2Cl_2	20
10	1,4-dioxane instead of CH_2Cl_2	36
11	THF instead of CH_2Cl_2	34
12	1,2-dichloroethane instead of CH_2Cl_2	0
13	With H_2O (10 equiv)	72
14	In dark	0
15	No [Ir] catalyst	0
16	No ETCA	0
17[c]	36 ºC	82

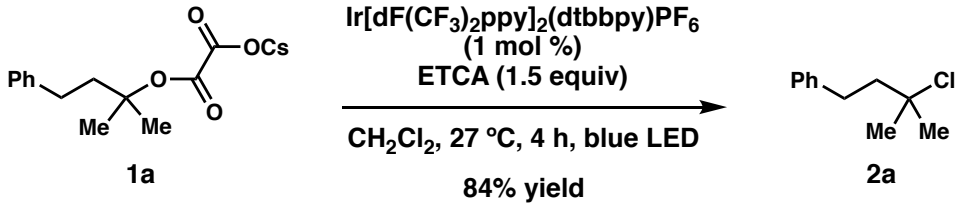
[a]Performed on 37 mg (0.1 mmol) scale ETCA = ethyl trichloroacetate, HCA = hexachloroacetone, **A** = ethyl chloroacetate, **B** = diethyl 2-chloromalonate, **C** = dimethyl 2,2-dichloromalonate. Internal temperature measured using a thermocouple as 27 °C.
[b]Yields determined by quantitative ^{1}H NMR spectrometry using pyrazine as a standard.
[c]Reaction directly irradiated with a Kessil A160WE blue LED lamp ~ 4 cm away. Internal temperature measured using a thermocouple.

General Procedure #1 (reaction optimization): On a benchtop, 1 dram vials each containing a stir bar were successively charged with cesium oxalate **1a** (37 mg, 0.10 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.1 mg, 0.001 mmol, 0.01 equiv), degassed solvent (0.5 mL) that was sparged with a balloon of argon for 15 min, and chlorinating agent (0.15 mmol, 1.5 equiv). The vials were sparged with argon for an additional 10–15 seconds and then sealed under a stream of argon with a screw cap. The vials were subsequently irradiated with blue LED light for 4 h in a Hepatochem device. Following this time, each of the vials was removed from the Hepatochem

device. A 1:1 mixture of a saturated aqueous solution of NaCl and H_2O (1.5 mL) was added to each vial and then each reaction was extracted with Et_2O (3 x 3 mL). Each of the combined organic extracts was dried over $MgSO_4$, filtered, and concentrated under rotary evaporation in a rotavap water bath at 27 °C (at a pressure of ~60–100 mmHg for volatile products). NMR yields were determined using quantitative ^1H NMR spectroscopy with pyrazine as an added standard. The ^1H NMR data for tertiary chloride **2a** was consistent with those reported in the literature.[8]

General Procedure #2 (substrate scope): On a benchtop, a 20 mL scintillation vial containing a stir bar was successively charged with cesium oxalate (1 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.01 equiv), degassed CH_2Cl_2 (1.5 mL, sparged with a balloon of argon for 15 min), and ETCA (1.5 equiv). The vial was sparged with argon for an additional 10–15 seconds and then sealed under a stream of argon with a screw cap. The vial was placed in a Hepatochem device and irradiated with blue LED light. Tertiary alcohol-derived cesium oxalates were irradiated for 4 h and secondary alcohol-derived cesium oxalates were irradiated for 24 h. The vial was subsequently removed from the Hepatochem device and transferred to a separatory funnel with a 1:1 mixture of a saturated aqueous solution of NaCl and H_2O (1.5 mL). The mixture was extracted with Et_2O (3 x 3 mL) and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under rotary evaporation in a rotavap water bath at 27 °C (at a pressure of ~60–100 mmHg for volatile products). The crude residue was purified by silica gel chromatography to afford the chlorinated products. To mitigate elimination of tertiary chlorides to the corresponding alkenes during purification, silica gel columns were treated with Et_3N as needed for selected products (see below).

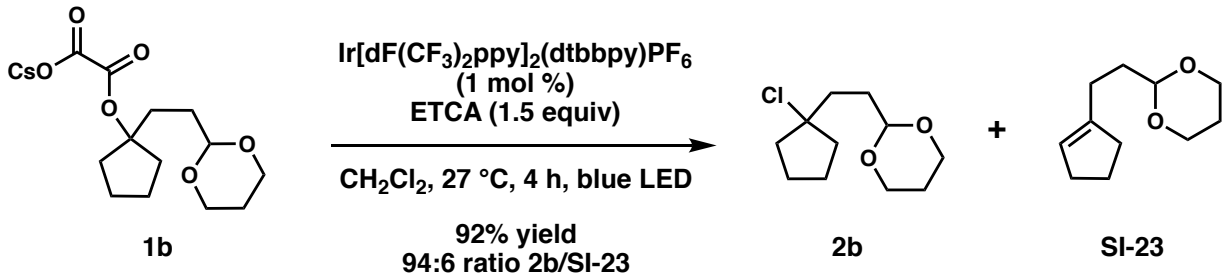
Chlorides **2a**, **2b**, **2c**, **2d**, **2f**, **2i**, and **2o** were contaminated with ETCA following purification by column chromatography. For these products, the remaining ETCA was removed by dissolving in THF (0.9 mL) and MeOH (0.45 mL), cooling to 0 ºC, and then adding a 3 M aqueous solution of NaOH (0.3 mL) dropwise. After stirring at 0 ºC for 5 min and room temperature for 25 min, the solution was diluted with H_2O (1 mL) and extracted with Et_2O (4 x 2 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford the chloride products.



(3-chloro-3-methylbutyl)benzene (2a): Prepared according to general procedure #2 using cesium oxalate **1a** (115 mg, 0.31 mmol).[2] Purification of the orange-colored crude residue by silica gel

column chromatography (0–2% Et_2O/pentane). Residual ETCA was removed by treatment with aqueous NaOH according to general procedure #2 to provide chloride **2a** as a pale yellow oil (48 mg, 84% yield). The ^1H NMR data for tertiary chloride **2a** was consistent with those reported in the literature.[8]

TLC R_f = 0.34 (hexanes, *p*-anisaldehyde)



1b 2b SI-23

2-(2-(1-chlorocyclopentyl)ethyl)-1,3-dioxane (2b): Prepared according to general procedure #2 using cesium oxalate **1b** (119 mg, 0.29 mmol). A silica gel column was eluted with two column volumes of 3% Et_3N/5% Et_2O/pentane. Purification of the crude residue was then performed on this column (5–15% Et_2O/pentane). Residual ETCA was removed by treatment with aqueous NaOH according to general procedure #2 to furnish a 94:6 mixture of chloride **2b** and alkene **SI-23** as pale yellow oil (61 mg, 92% yield: 87% **2b**, 5% **SI-23**). ^1H NMR analysis indicated that alkene **SI-23** did not form until after the NaOH hydrolysis procedure.

TLC R_f (2b)= 0.37 (15% Et_2O/pentane, *p*-anisaldehyde).

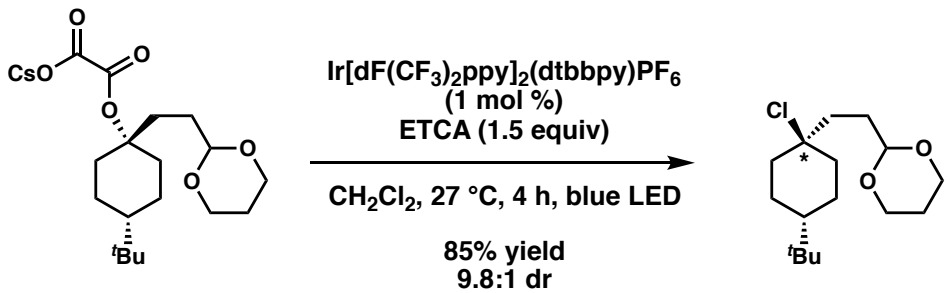
TLC R_f (SI-23)= 0.43 (15% Et_2O/pentane, *p*-anisaldehyde).

^1H NMR (**2b**, 400 MHz, $CDCl_3$) δ 4.55 (t, *J* = 4.6 Hz, 1H), 4.09 (ddt, *J* = 10.5, 5.0, 1.4 Hz, 2H), 3.83 – 3.67 (m, 2H), 2.15 – 1.99 (m, 3H), 1.99 – 1.82 (m, 6H), 1.78 – 1.62 (m, 4H), 1.33 (dtt, *J* = 13.5, 2.6, 1.4 Hz, 1H).

^{13}C NMR (**2b**, 101 MHz, $CDCl_3$) δ 102.1, 82.7, 67.0, 42.4, 37.5, 31.9, 25.9, 23.2.

FTIR (NaCl, thin film, cm^{-1}): 2964, 2850, 2730, 2657, 1449, 1406, 1378, 1241, 1146, 1080, 998.

HRMS (FAB+, *m/z*): calc'd for $C_{11}H_{18}ClO_2$ $(M+H-H_2)^+$: 217.0995, found: 217.0983.



1c 2c

2-(2-((1*r*,4*r*)-4-(*tert*-butyl)-1-chlorocyclohexyl)ethyl)-1,3-dioxane (2c): Prepared according to general procedure #2 using cesium oxalate **1c** (140 mg, 0.30 mmol). A silica gel column was eluted with two column volumes of 3% Et_3N/2% Et_2O/pentane. Purification of the crude residue was then performed on this column (5–10% pentane/Et_2O). Residual ETCA was removed by treatment with aqueous NaOH according to general procedure #2 to give chloride **2c** as a 9.8:1 mixture of inseparable diastereomers as a clear colorless oil (72 mg, 85% yield).

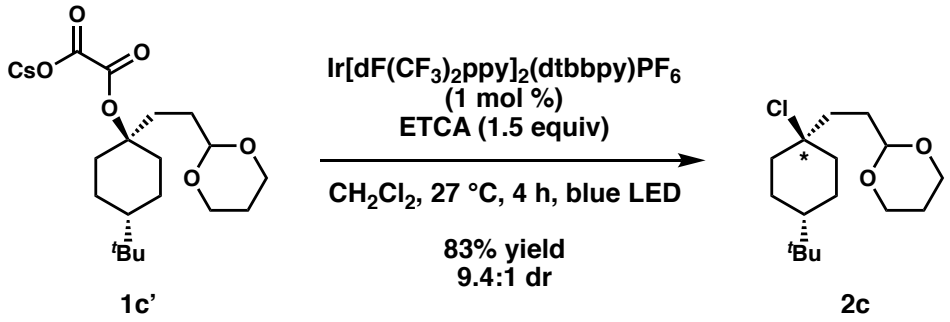
TLC R_f = 0.23 (10% Et_2O/hexanes, $KMnO_4$).

^{1}H NMR (major diastereomer, 400 MHz, $CDCl_3$) δ 4.55 (t, *J* = 4.5 Hz, 1H), 4.10 (ddt, *J* = 10.4, 5.0, 1.4 Hz,2H), 3.76 (dddd, *J* = 12.7, 10.5, 2.6, 1.5 Hz, 2H), 2.20 – 2.03 (m, 1H), 2.05 – 1.96 (m, 2H), 1.93 – 1.75 (m, 4H), 1.70 – 1.57 (m, 2H), 1.57 – 1.30 (m, 5H), 0.93 (tt, *J* = 11.8, 3.5 Hz, 1H), 0.86 (s, 9H).

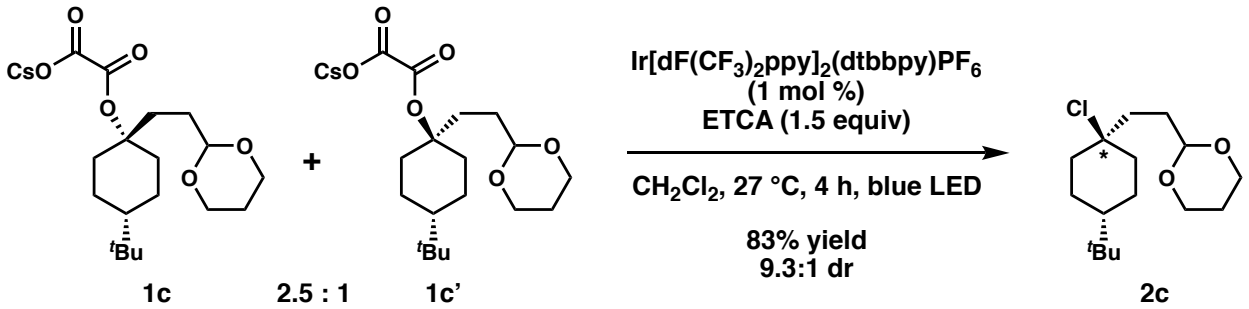
^{13}C NMR (major diastereomer, 101 MHz, $CDCl_3$) δ 102.4, 75.5, 67.1, 47.7, 40.2, 40.1, 32.6, 30.0, 27.7, 25.9, 23.0.

FTIR (NaCl, thin film, cm^{-1}): 2947, 2849, 2730, 2658, 1448, 1404, 1366, 1287, 1240, 1147, 1079, 1042, 1009, 975.

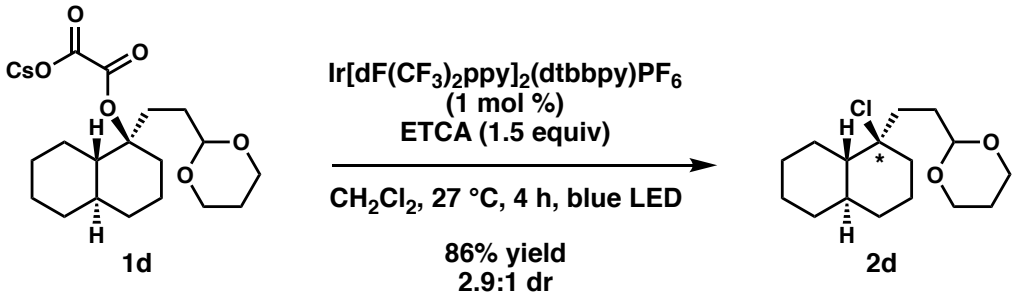
HRMS (FAB+, *m/z*): calc'd for $C_{16}H_{28}ClO_2$ $(M+H-H_2)^+$: 287.1778, found: 287.1755.



2-(2-((1*r*,4*r*)-4-(*tert*-butyl)-1-chlorocyclohexyl)ethyl)-1,3-dioxane (2c): Prepared according to general procedure #2 using the epimer of cesium oxalate **1c**, cesium oxalate **1c'** (114 mg, 0.24 mmol). Purification of the crude residue was then performed as above to provide chloride **2c** as a 9.4:1 mixture of inseparable diastereomers as a clear colorless oil (58 mg, 83% yield).



2-(2-((1*r*,4*r*)-4-(*tert*-butyl)-1-chlorocyclohexyl)ethyl)-1,3-dioxane (2c): Prepared according to the general procedure #2 using a 2.5:1 mixture of cesium oxalates **1c** and **1c'** respectively (139 mg, 0.29 mmol). Purification of the crude residue was then performed as above to give chloride **2c** as a 9.3:1 mixture of inseparable diastereomers as a clear colorless oil (70 mg, 83% yield).



2-(2-((1*R*,4a*R*,8a*S*)-1-chlorodecahydronaphthalen-1-yl)ethyl)-1,3-dioxane (2d): Prepared according to general procedure #2 using cesium oxalate **1d** (147 mg, 0.31 mmol). A silica gel column was eluted with two column volumes of 3% Et_3N/5% Et_2O/pentane. Purification of the crude residue was then performed on this column (5–15% pentane/Et_2O). Residual ETCA was removed by treatment with aqueous NaOH according to general procedure #2 to deliver chloride **2d** as a 2.9:1 mixture of inseparable diastereomers as a clear colorless oil (77 mg, 86% yield).

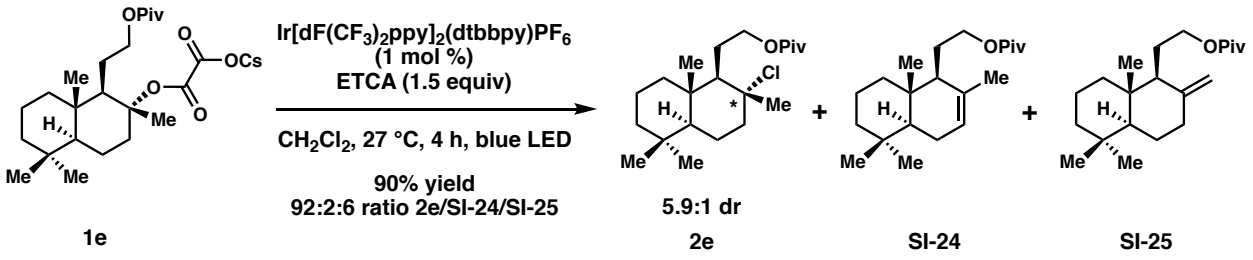
TLC R_f = 0.29 (15% Et_2O/pentane, *p*-anisaldehyde).

^{1}H NMR (2.4:1 dr, asterisk denotes minor diastereomer, 400 MHz, $CDCl_3$) δ *4.55 – 4.53 (m, 0.3H), 4.51 (dd, *J* = 5.5, 4.1 Hz, 1H), 4.10 (ddq, *J* = 10.2, 5.0, 1.8, 1.4 Hz, 2.7H), 3.85 – 3.67 (m, 2.7H), *2.30 – 2.20 (m, 0.5H), 2.16 – 1.96 (m, 2.8H), 1.98 – 1.87 (m, 1.6H), 1.87 – 1.70 (m, 6.4H), 1.70 – 1.40 (m, 9.6H), 1.40 – 1.08 (m, 7.7H), 1.08 – 0.77 (m, 4.3H).

^{13}C NMR (asterisk denotes minor diastereomer, 101 MHz, $CDCl_3$) δ *102.5, 102.4, *79.8, 79.0, 67.1, *55.8, 51.1, *40.5, *39.8, 38.9, 37.0, *35.0, 34.6, 34.0, *33.9, 30.2, *29.9, *28.1, *26.9, *26.7, 26.6, 26.3, 26.1, *25.93, 25.91, *23.3, 21.9.

FTIR (NaCl, thin film, cm^{-1}): 2928, 2850, 2730, 2662, 1449, 1404, 1377, 1286, 1244, 1144, 1076, 1001.

HRMS (FAB+, *m/z*): calc'd for $C_{16}H_{26}ClO_2$ $(M+H-H_2)^+$: 285.1621, found: 285.1650.



1e 2e SI-24 SI-25

2-((1*R*,2*R*,4a*S*,8a*S*)-2-chloro-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)ethyl pivalate (2e): Prepared according to general procedure #2 using cesium oxalate **1e** (165 mg, 0.30 mmol). A silica gel column was eluted with two column volumes of 3% Et_3N/2% Et_2O/pentane. Purification of the crude residue was then performed on this column (isocratic: 2% Et_2O/hexanes) to afford a 92:2:6 mixture of chloride **2e**, alkene **SI-24**, and alkene **SI-25** as a viscous yellow oil (96 mg, 90% yield: 83% **2e** 5.9:1 dr, 2% **SI-24**, 5% **SI-25**).

TLC R_f (2e) = 0.28 (3% Et_2O/pentane, *p*-anisaldehyde).

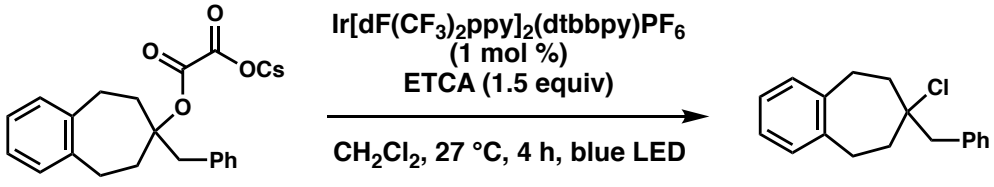
$[\alpha]_D^{25}$ = +3.6° (c = 1.01, $CHCl_3$).

^{1}H NMR (**2e**, asterisk denotes minor diastereomer, 400 MHz, $CDCl_3$) δ 4.17 (td, *J* = 10.3, 6.0 Hz, 1H), 4.07 (td, *J* = 10.2, 6.1 Hz, 1H), *4.05 – 3.98 (m, 0.34 H), (dt, *J* = 12.9, 3.3 Hz, 1H), 2.12 – 1.98 (m, 1H), 1.92 – 1.75 (m, 1H), 1.74 – 1.61 (m, 3H), 1.59 – 1.51 (m, 4H), 1.52 – 1.24 (m, 3H), 1.19 (d, *J* = 1.6 Hz, 11H), 1.16 – 1.07 (m, 1H), 1.05 – 0.90 (m, 3H), 0.86 (d, *J* = 1.7 Hz, 4H), 0.85 – 0.79 (m, 3H), 0.77 (s, 3H).

^{13}C NMR (**2e**, asterisk denotes minor diastereomer, 101 MHz, $CDCl_3$) δ *178.83, 178.80, 78.0, *75.7, 66.4, *66.0, 58.9, *57.2, *56.1, 56.0, 46.5, *45.2, *42.0, 41.8, 40.7, 39.9, *39.6, *39.4, 38.83*, 38.82, *34.3, *33.5, 33.4, 33.3, 27.4, *26.9, *26.4, 26.2, *21.8, 21.6, 21.1, *18.8, 18.4, *18.2, 15.7, *15.5.

FTIR (NaCl, thin film, cm^{-1}): 2953, 1728, 1480, 1460, 1390, 1366, 1284, 1230, 1157, 1056, 1035, 979.

HRMS (EI, *m/z*): calc'd for $C_{21}H_{37}O_2Cl$ $(M+\cdot)^+$: 356.2480, found: 356.2482.



1f 2f

7-benzyl-7-chloro-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (2f): Prepared according to general procedure #2 using cesium oxalate **1f** (139 mg, 0.31 mmol). A silica gel column was eluted with two column volumes of 2% Et_3N/hexanes. Purification of the crude material was then performed on this column (isocratic: 2% Et_2O/hexanes). Residual ETCA was removed by treatment with

aqueous NaOH according to general procedure #2 to give chloride **2f** as a white crystalline solid (55 mg, 67% yield).

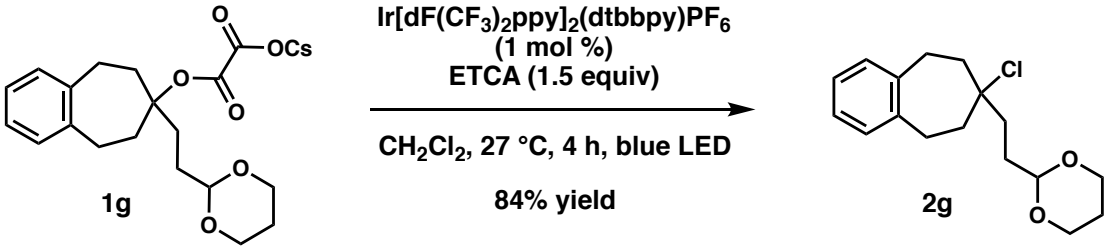
TLC R_f = 0.35 (3% Et_2O/pentane, *p*-anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.17 (m, 5H), 7.09 (d, *J* = 1.1 Hz, 4H), 3.32 (t, *J* = 13.4 Hz, 2H), 3.09 (s, 2H), 2.58 (dd, *J* = 14.9, 7.0 Hz, 2H), 2.27 – 2.06 (m, 2H), 1.72 (t, *J* = 13.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 136.1, 131.4, 129.0, 128.0, 127.0, 126.4, 78.9, 53.0, 41.0, 31.0.

FTIR (NaCl, thin film, cm^{-1}): 3062, 3028, 2935, 2856, 1948, 1881, 1806, 1604, 1494, 1453, 1208, 1187, 1080, 1037.

HRMS (EI, *m/z*): calc'd for $C_{18}H_{19}Cl$ $(M+\cdot)^+$: 270.1175, found: 270.1169.



2-(2-(7-chloro-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-7-yl)ethyl)-1,3-dioxane (2g): Prepared according to general procedure #2 using cesium oxalate **1g** (149 mg, 0.31 mmol). A silica gel column was eluted with two column volumes of 2% Et_3N/5% Et_2O/hexanes. Purification of the crude material was then performed on this column (3–5% EtOAc/hexanes) to afford chloride **2g** as a viscous yellow oil (76 mg, 84% yield).

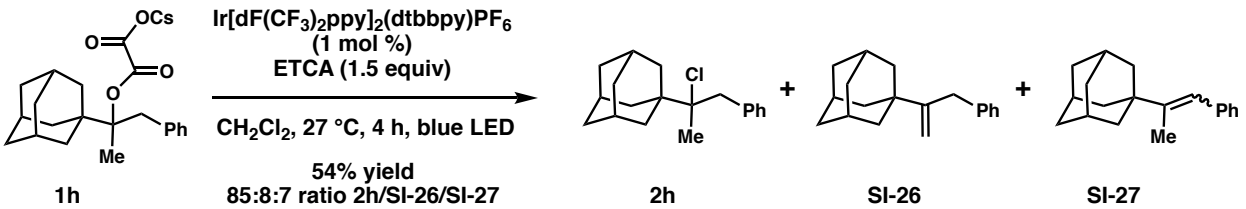
TLC R_f = 0.21 (5% EtOAc/hexanes, *p*-anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 4H), 4.65 – 4.48 (m, 1H), 4.10 (ddt, *J* = 10.4, 5.0, 1.4 Hz, 2H), 3.86 – 3.61 (m, 2H), 3.15 – 3.45 (br d, *J* = 14.4 Hz, 2H), 2.75 – 2.47 (m, 2H), 2.27 – 2.15 (m, 2H), 2.07 (dtt, *J* = 13.5, 12.5, 5.0 Hz, 1H), 1.97 – 1.80 (m, 4H), 1.66 (d, *J* = 14.0 Hz, 2H), 1.40 – 1.29 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 128.9, 126.4, 102.2, 79.1, 67.0, 41.1, 31.0, 30.1, 25.9.

FTIR (NaCl, thin film, cm^{-1}): 2938, 2852, 1764, 1493, 1453, 1404, 1377, 1239, 1145, 1086, 1004.

HRMS (EI, *m/z*): calc'd for $C_{17}H_{22}O_2Cl$ $(M+H-H_2)^+$: 293.1308, found: 293.1322.



(3*r*,5*r*,7*r*)-1-(2-chloro-1-phenylpropan-2-yl)adamantine (2h): Prepared according to general

procedure #2 using cesium oxalate **1h** (146 mg, 0.31 mmol). A silica gel column was eluted with two column volumes of 2% Et_3N/pentane. Purification of the crude residue was then performed on this column (isocratic: 2% Et_2O/pentane) to afford an inseparable 85:8:7 mixture of chloride **2h**, alkene **SI-26**, and alkene **SI-27** as a white crystalline solid (49 mg, 54% yield: 46% **2h**, 4% **SI-26**, 4% **SI-27**).

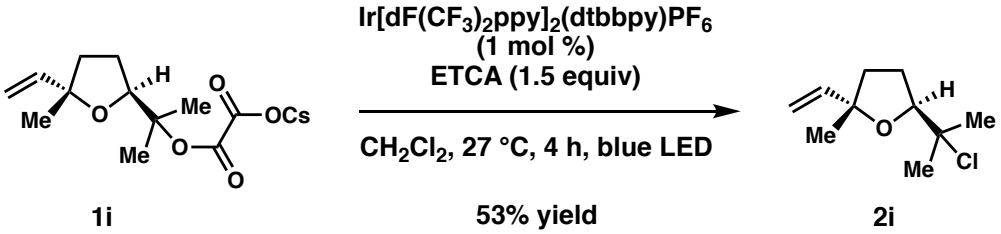
TLC R_f = 0.43 (2% EtOAc/hexanes, $KMnO_4$).

^{1}H NMR (**2h**, 400 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 5H), 3.19 (d, *J* = 13.7 Hz, 1H), 2.91 (d, *J* = 13.7 Hz, 1H), 2.13 – 1.96 (m, 3H), 1.88 (d, *J* = 3.0 Hz, 6H), 1.82 – 1.58 (m, 9H), 1.29 (d, *J* = 0.8 Hz, 3H).

^{13}C NMR (**2h**, 101 MHz, $CDCl_3$) δ 137.8, 131.8, 127.7, 126.6, 82.6, 43.0, 41.2, 37.1, 37.0, 28.9, 23.1.

FTIR (NaCl, thin film, cm^{-1}): 2905, 2849, 1763, 1604, 1496, 1451, 1082, 972.

HRMS (TOF-ES+, *m/z*): calc'd for $C_{19}H_{25}ClH$ $(M+H)^+$: 289.1718, found: 289.1723.



1i **53% yield** **2i**

(2*S*,5*S*)-5-(2-chloropropan-2-yl)-2-methyl-2-vinyltetrahydrofuran (2i): Prepared according to general procedure #2 using cesium oxalate **1i** (126 mg, 0.34 mmol). The crude residue was purified by silica gel chromatography (3–5% Et_2O/pentane). Residual ETCA was removed by treatment with aqueous NaOH according to general procedure #2 to provide chloride **2i** as a white crystalline solid (33.4 mg, 53% yield).

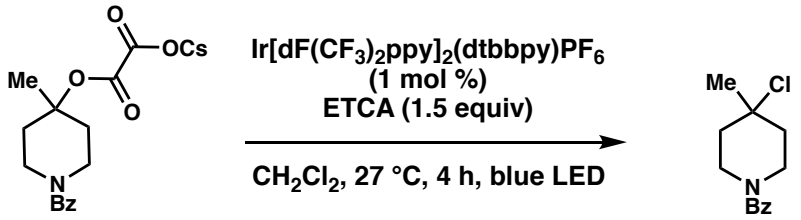
TLC R_f = 0.37 (3% Et_2O/pentane, *p*-anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.18 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.00 (dd, *J* = 10.6, 1.6 Hz, 1H), 3.98 (dd, *J* = 7.4, 6.1 Hz, 1H), 2.03 – 1.93 (m, 2H), 1.88 (ddd, *J* = 12.0, 8.0, 4.9 Hz, 1H), 1.81 – 1.68 (m, 1H), 1.55 (d, *J* = 1.5 Hz, 6H), 1.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 111.6, 85.8, 84.1, 71.5, 37.1, 29.9, 27.8, 27.7, 26.7.

FTIR (NaCl, thin film, cm^{-1}): 3088, 2979, 2871, 1750, 1643, 1461, 1386, 1369, 1302, 1242, 1119, 1063, 1028, 921.

HRMS (GC-EI, *m/z*): calc'd for $C_{10}H_{17}OCl$ $(M+H-H_2)^+$: 188.0943, found: 188.0968.



1j **55% yield** **2j**

(4-chloro-4-methylpiperidin-1-yl)(phenyl)methanone (2j): Prepared according to general procedure #2 using cesium oxalate **1j** (146 mg, 0.31 mmol). The crude residue was purified by silica gel chromatography (10–40% EtOAc/hexanes), furnishing **2j** as a light yellow solid (41 mg, 55% yield).

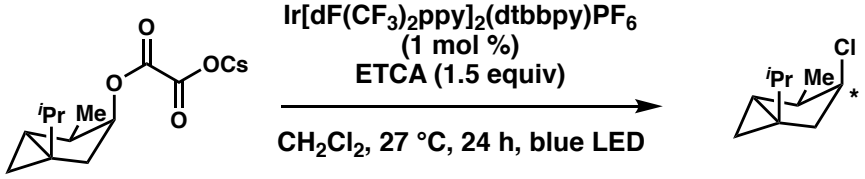
TLC R_f = 0.28 (33% EtOAc/hexanes, UV, $KMnO_4$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 5H), 4.49 – 4.68 (br d, *J* = 13.4 Hz, 1H), 3.55 – 3.73 (br s, 1H), 3.55 – 3.37 (m, 1H), 3.34 – 3.11 (br s, 1H), 2.11 – 1.90 (m, 1H), 1.92 – 1.73 (m, 2H), 1.73 – 1.55 (m, 1H), 1.66 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 136.0, 129.8, 128.6, 127.0, 69.3, 44.5, 41.2, 40.3, 38.8, 33.4.

FTIR (NaCl, thin film, cm^{-1}): 3059, 2946, 2873, 1634, 1578, 1433, 1372, 1288, 1254, 1168, 1130, 1107, 967.

HRMS (TOF-ESI, *m/z*): calc'd for $C_{13}H_{16}ClNOH^+$ $(M+H)^+$: 238.0993, found: 238.0986.



1k **50% yield** **20:1 dr** **2k**

(1*S*,3*R*,4*R*,5*R*)-3-chloro-1-isopropyl-4-methylbicyclo[3.1.0]hexane (2k): Prepared according to general procedure #2 using cesium oxalate **1k** (114 mg, 0.32 mmol). The crude residue was purified by silica gel chromatography (isocratic: hexanes) to afford chloride **2k** as a fragrant clear colorless oil (27.4 mg, 50% yield, 20:1 dr). The spectral data was consistent with those reported in the literature.[9]

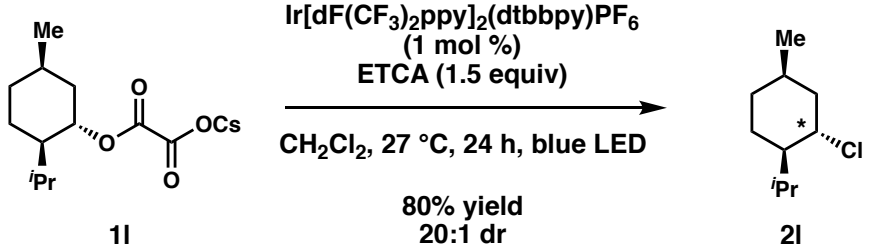
TLC R_f = 0.70 (pentane, *p*-anisaldehyde).

$[\alpha]_D^{25}$ = –18.5° (c = 0.96, $CHCl_3$).

^{1}H NMR (19:1 dr, major diastereomer, 400 MHz, $CDCl_3$) δ 3.95 – 3.80 (m, 1H), 2.38 (ddd, *J* = 14.5, 7.9, 1.9 Hz, 1H), 2.17 (qd, *J* = 7.1, 3.0 Hz, 1H), 1.79 (dd, *J* = 14.4, 3.5 Hz, 1H), 1.28 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.06 (d, *J* = 7.2 Hz, 3H), 0.98 – 0.94 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.86 (ddt, *J* = 8.4, 3.9, 1.0 Hz, 1H), 0.57 (ddd, *J* = 8.4, 4.8, 1.7 Hz, 1H).

^{13}C NMR (19:1 dr, major diastereomer, 101 MHz, $CDCl_3$) δ 65.7, 47.2, 38.0, 35.2, 33.1, 29.9, 20.7, 20.3, 19.9, 19.0.

FTIR (NaCl, thin film, cm^{-1}): 2959, 2872, 1458, 1382, 1298, 1252, 1064, 1032, 940.



1l **2l**

(1*R*,2*S*,4*R*)-2-chloro-1-isopropyl-4-methylcyclohexane (2l): Prepared according to general procedure #2 using cesium oxalate **1l** (110 mg, 0.31 mmol). The crude residue was purified by silica gel chromatography (isocratic: pentane) to furnish chloride **2l** as a clear colorless oil (42.5 mg, 80% yield, 20:1 dr).

TLC R_f = 0.90 (pentane, *p*-anisaldehyde).

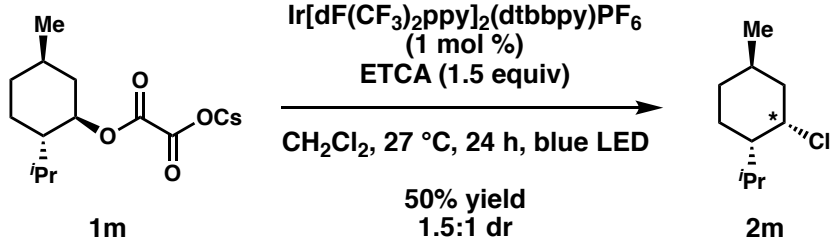
$[\alpha]_D^{25}$ = +31.8° (c = 0.95, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (td, *J* = 7.5, 4.0 Hz, 1H), 2.02 (ddt, *J* = 14.2, 7.3, 5.0 Hz, 2H), 1.91 – 1.76 (m, 2H), 1.76 – 1.65 (m, 1H), 1.60 – 1.37 (m, 2H), 1.36 – 1.19 (m, 2H), 0.93 (dd, *J* = 6.9, 1.6 Hz, 6H), 0.86 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 62.0, 49.9, 41.1, 30.3, 28.0, 27.4, 21.1, 20.5, 19.9, 18.2.

FTIR (NaCl, thin film, cm^{-1}): 2959, 2928, 2872, 1461, 1386, 1210, 1022, 975.

HRMS (GC-EI, *m/z*): calc'd for $C_{10}H_{19}Cl$ $(M+\cdot)^+$: 174.1175, found: 174.1162.

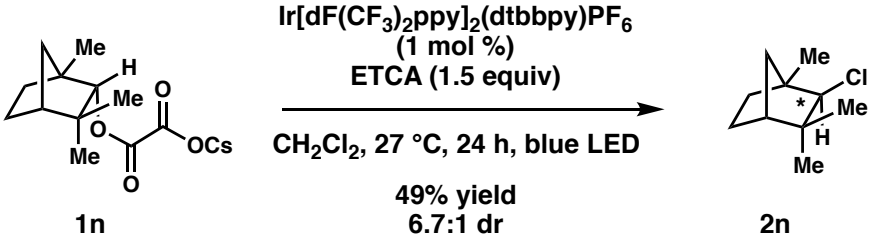


1m **2m**

(1*S*,2*S*,4*R*)-2-chloro-1-isopropyl-4-methylcyclohexane (2m): Prepared according to general procedure #2 using cesium oxalate **1m** (108.5 mg, 0.30 mmol). The crude residue was purified by silica gel chromatography (isocratic: pentane) to afford chloride **2m** as a clear colorless oil (25.3 mg, 50% yield, 1.5:1 dr). The ^{1}H NMR spectrum of the mixture of diastereomers was consistent with those reported for the individual diastereomers, neomenthyl chloride[10] and commercially available (−)-menthyl chloride.

TLC R_f = 0.72 (pentane, *p*-anisaldehyde).

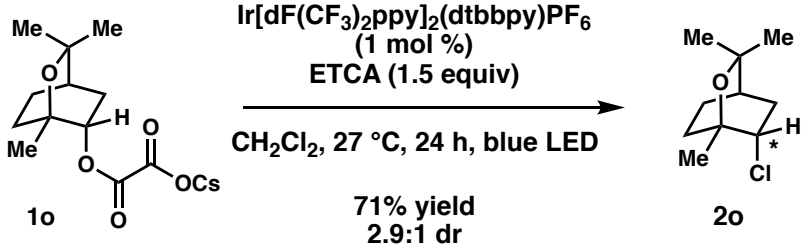
FTIR (NaCl, thin film, cm^{-1}): 2956, 2928, 2870, 1454, 1370, 1278.



(1*S*,2*R*,4*R*)-2-chloro-1,3,3-trimethylbicyclo[2.2.1]heptane (2n): Prepared according to general procedure#2 using cesium oxalate **1n** (109 mg, 0.30 mmol). The crude residue was purified by silica gel chromatography (isocratic: pentane) to provide chloride **2n** as a clear colorless oil (25.5 mg, 49% yield, 6.7:1 dr). The ^{1}H NMR spectrum of the mixture of diastereomers was consistent with those reported in the literature for each of the individual diastereomers.[11]

TLC R_f = 0.93 (pentane, *p*-anisaldehyde).

FTIR (NaCl, thin film, cm^{-1}): 2953, 2870, 1468, 1366, 1274, 906.



(1*S*,4*R*,6*S*)-6-chloro-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane (2o): Prepared according to the general procedure using cesium oxalate **1o** (117 mg, 0.31 mmol). The crude residue was purified by silica gel chromatography (3–10% Et_2O/pentane). Residual ETCA was removed by treatment with aqueous NaOH according to general procedure #2 to afford chloride **2o** as a clear colorless fragrant oil (41.7 mg, 71% yield, 2.9:1 dr). The spectral data were consistent with those reported in the literature.[12]

TLC R_f (major diastereomer)= 0.29 (3% Et_2O/pentane, *p*-anisaldehyde).

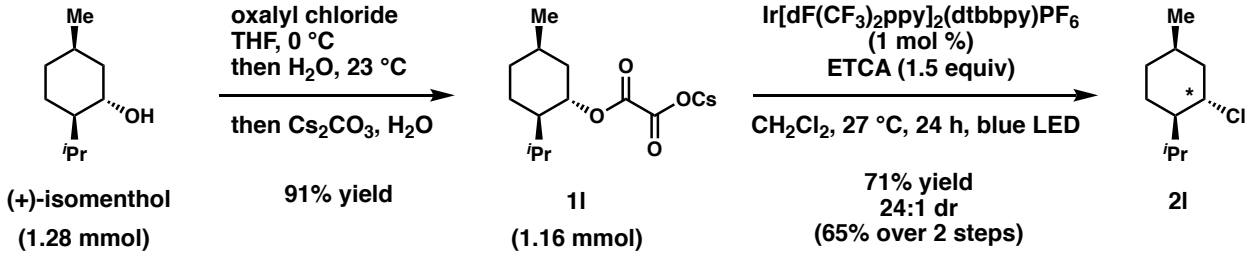
TLC R_f (minor diastereomer) = 0.24 (3% Et_2O/pentane, *p*-anisaldeyde).

^{1}H NMR (major diastereomer, 400 MHz, $CDCl_3$) δ 3.94 (ddd, *J* = 10.2, 4.4, 2.0 Hz, 1H), 2.74 (ddt, *J* = 14.8, 10.2, 3.4 Hz, 1H), 2.15 – 2.02 (m, 1H), 2.02 – 1.86 (m, 1H), 1.81 (ddd, *J* = 14.8, 4.4, 2.7 Hz, 1H), 1.69 – 1.56 (m, 2H), 1.54 (tt, *J* = 3.5, 2.4 Hz, 1H), 1.28 (s, 3H), 1.20 (d, *J* = 0.7 Hz, 3H), 1.17 (s, 3H).

^{13}C NMR (major diastereomer, 101 MHz, $CDCl_3$) δ 74.2, 73.5, 59.7, 36.3, 34.6, 28.9, 28.4, 25.4, 25.2, 21.9.

FTIR (NaCl, thin film, cm^{-1}): 3362, 2970, 2935, 1723, 1460, 1379, 1200, 1129, 1090, 1069, 1051, 987.

4. 1.3 mmol Scale Deoxychlorination Sequence.

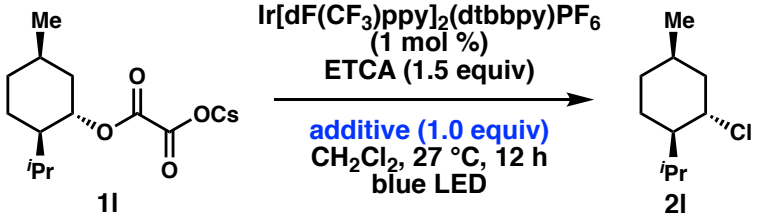


cesium 2-(((1*S*,2*R*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)-2-oxoacetate (1l): A flame-dried 100 mL round bottom flask attached to a 10 mL dropping funnel was charged with a solution of oxalyl chloride (0.11 mL, 1.29 mmol, 1.01 equiv) in THF (6.0 mL). The solution was cooled to 0 ºC followed by dropwise addition of a solution of (+)-isomenthol (200 mg, 1.28 mmol) in THF (6 mL) over 15 min. The transfer was made quantitative using an additional amount of THF (2 x 0.5 mL). After the reaction was stirred at this temperature for 1 h, H_2O (4.3 mL) was added and the resulting solution was warmed to room temperature while stirring for an additional 1 h. A saturated aqueous solution of NaCl (8 mL) was added, the contents were transferred to a separatory funnel, and the flask was rinsed with THF (2 mL) to make the transfer quantitative. The aqueous layer was separated and the organic layer was washed with a 2:1 mixture of a saturated aqueous solution of NaCl and H_2O (12 mL) followed by a 1:2 mixture of saturated aqueous solution of NaCl and H_2O (2 x 12 mL). A solution of Cs_2CO_3 (213 mg, 0.51 equiv) in H_2O (1.0 mL) was then added. The contents were shaken thoroughly and then concentrated under rotary evaporation to remove the THF. The aqueous solution was washed with 1:1 pentane/Et_2O (3 x 3 mL) and then concentrated using rotary evaporation followed by high vacuum (~50 mTorr) to afford cesium oxalate **1l** (419 mg, 91% yield) as a white solid.

(1*S*,2*S*,4*R*)-2-chloro-1-isopropyl-4-methylcyclohexane (2l): A 15 mL Schlenk tube was charged with cesium oxalate **1l** (419 mg, 1.16 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (13 mg, 0.012 mmol, 0.01 equiv), and a magnetic stir bar. The flask was evacuated and backfilled with argon (x 3) and CH_2Cl_2 (5.8 mL) that was degassed by sparging with argon for 15 min and ETCA (0.24 mL, 1.74 mmol, 1.5 equiv) were added. The flask was sealed and irradiated with a Kessil A160WE blue LED lamp placed approximately 4 cm away and cooled using a fan. The reaction was stirred vigorously for 24 h under these conditions (550 rpm). The blue LED was turned off and H_2O (5 mL) was added to the orange suspension. The contents were transferred to a separatory funnel and extracted with Et_2O (4 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under rotary evaporation in a rotavap water bath at 27 °C (at a pressure of ~60–

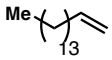
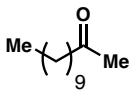
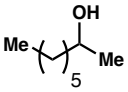
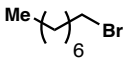
100 mmHg). The crude orange material was purified by silica gel chromatography (isocratic: pentane) to afford chloride **2l** as a clear colorless oil (144 mg, 71% yield, 24:1 dr).

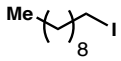
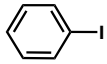
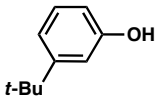
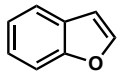
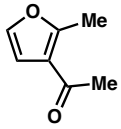
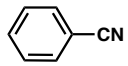
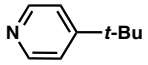
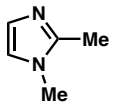
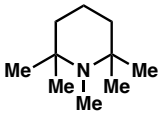
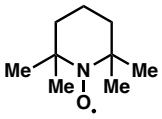
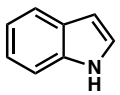
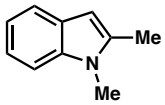
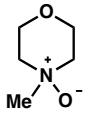
5. Functional Group Tolerance of the Radical Deoxychlorination.



General Procedure #3: On a benchtop, 1/2 dram vials each containing a stir bar were successively charged with **1l** (37 mg, 0.10 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (1.2 mg, 0.001 mmol, 0.01 equiv), additive (0.10 mmol, 1.0 equiv), CH_2Cl_2 (0.5 mL) that was degassed by sparging with a balloon of argon for 15 min, and ETCA (29 mg, 0.15 mmol, 1.5 equiv). The vials were sparged with argon for an additional 5 seconds, sealed under a stream of argon, and irradiated with blue LED light in a Hepatochem device for 12 h. After removing the vials from the Hepatochem device, a 1:1 mixture of saturated aqueous solution of NaCl and H_2O (0.5 mL) was added to each vial. Each reaction was extracted with Et_2O (4 x 1 mL). Each of the combined organic extracts was then dried over $MgSO_4$ and filtered. A solution of a measured amount of *n*-dodecane standard in hexanes was added to each of the combined organic extracts. After thoroughly mixing the resulting solutions, a ~1 mL aliquot was taken for each sample and analyzed by GC-flame ionization detection. The yields of **2l** and additive were calculated based on a calibrated response factor (RF).

Response Factor (RF) = (Area standard/Area additive) x (mmol additive/mmol standard)
RF **2l** (major diastereomer) = 1.209 RF **2l** (minor diastereomer) = 1.553

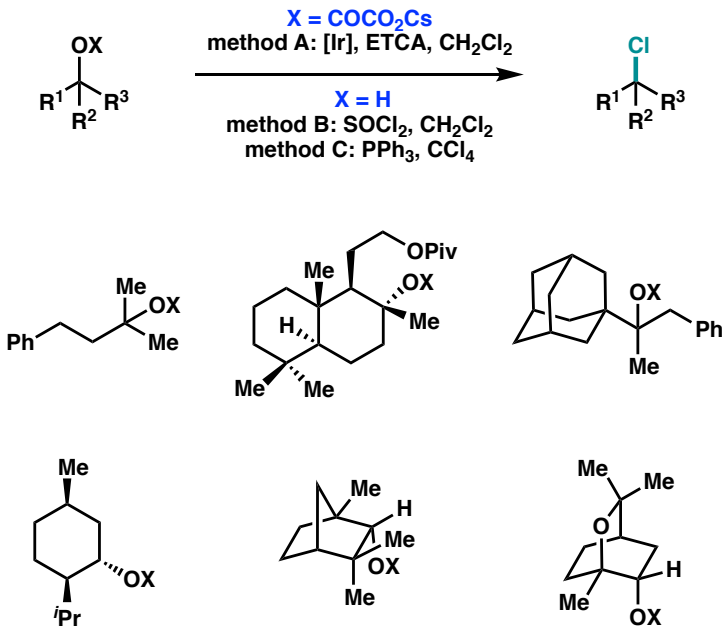
Additive	Area % 2l[a]	Area % std	Area % additive	RF additive:std	Mass std (mg)	GC yield of 2l	Additive recovery
None	55.7	24.3	N/A	N/A	5.0	80%	N/A
	36.8	18.3	31.6	1.065	4.6	64%	48%
	30.6	16.2	34.9	1.237	5.7	76%	87%
	36.8	16.8	22.5	2.426	5.3	80%	97%
	31.8	15.3	33.1	1.564	5.3	76%	101%

	30.7	16.5	33.4	1.563	4.9	65%	90%
	33.4	19.2	28.2	1.914	5.7	70%	92%
	0.7	44.0	13.4	1.586	5.3	1%	15%
	39.0	18.1	35.3	1.954	4.6	69%	99%
	42.1	19.5	24.7	2.291	4.6	69%	75%
	38.9	17.1	30.1	1.761	4.9	79%	87%
	17.3	31.1	32.3	1.432	5.7	72%	87%
	0.6	37.2	ND	ND	5.8	1%	ND[b]
	58.0	31.9	3.9	3.598	5.8	74%	14%
	3.9	50.7	0.6	1.379	4.9	3%	0%
	2.9	52.1	3.7	1.279	5.8	2%	3%
	0.0	48.0	10.0	2.165	5.7	0%	15%
	0.0	21.1	32.7	1.377	4.6	0%	55%
BF_3•OEt_2	1.4	35.3	ND	ND	4.9	2%	ND
	49.0	31.8	ND	ND	4.9	53%	ND

[a]Area % **2l** = combined area of major and minor diastereomers of **2l**

[b]Not determined due to overlapping peaks in GC trace.

6. Comparison with Non-Radical Deoxychlorination Processes.



Method A (Radical deoxychlorination conditions; X=$COCO_2Cs$): Experimental procedures listed in the above deoxychlorination reactions section.

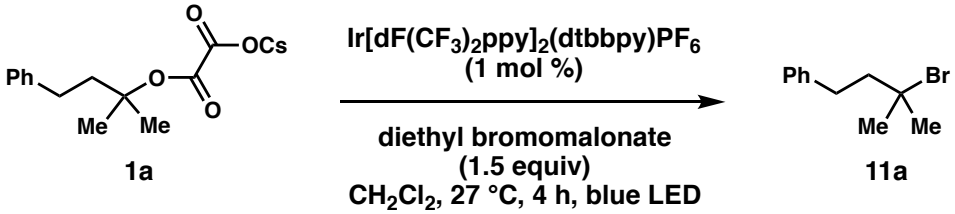
Method B (Appel reaction conditions; X=H): A 2 dram vial containing a stir bar was successively charged with alcohol substrate (0.1 mmol), triphenyl phosphine (52.5 mg, 0.2 mmol, 2.0 equiv), and CCl_4 (0.33 mL). The vial was sealed and the reaction contents were stirred at 70 ºC for 14 h. The reaction was then cooled to room temperature and diluted with Et_2O (2 mL). The resulting slurry was filtered through Celite, rinsed with Et_2O (10 mL), and concentrated under rotary evaporation in a rotavap water bath at 27 °C (at a pressure of ~60–100 mmHg for volatile products). NMR yields were determined using quantitative ^1H NMR spectroscopy with pyrazine as an added standard.

Method C ($SOCl_2$ conditions; X=H): A 2 dram vial containing a stir bar was successively charged with alcohol substrate (0.1 mmol) and CH_2Cl_2 (1.0 mL) and the contents were then placed under an argon atmosphere and cooled to 0 ºC. To the stirred solution was added $SOCl_2$ (35 µL, 0.50 mmol, 5.0 equiv) dropwise. The reaction was then allowed to warm to room temperature and stirred for 20 h. The reaction was slowly quenched with a 1:1 mixture of a saturated aqueous solution of NaCl and a saturated aqueous solution of $NaHCO_3$ (1.0 mL) and then extracted with Et_2O (4 x 3 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated

under rotary evaporation in a rotavap water bath at 27 °C (at a pressure of ~60–100 mmHg for volatile products). NMR yields were determined using quantitative ^{1}H NMR spectroscopy with pyrazine as an added standard.

7. Deoxybromination Reactions

Optimization of Reaction Parameters



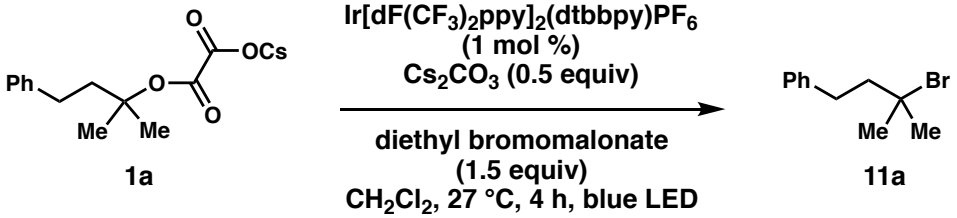
Entry[a]	Deviation from above conditions	NMR yield **11a** (%)[b]
1	None	66
2	NBS	0
3	CBr_4	4
4	1,1,2,2-tetrabromoethane	15
5	Ethyl tribromoacetate	9
6	2-bromo-2-methyl propionic acid	0
7	0.2 equiv Cs_2CO_3	80
8	**0.5 equiv Cs_2CO_3**	**89**
9	1.0 equiv C s_2CO_3	64

[a]Performed on 37 mg (0.1 mmol) scale.
[b]Yields determined by quantitative ^{1}H NMR spectrometry using pyrazine as a standard.

General Procedure #4 (reaction optimization): On a benchtop, 1 dram vials each containing a stir bar were successively charged with cesium oxalate **1a** (37 mg, 0.10 mmol, 1 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.1 mg, 0.001 mmol, 0.01 equiv), CH_2Cl_2 (0.5 mL) that was degassed by sparging with a balloon of argon for 15 min, and brominating agent (0.15 mmol, 1.5 equiv). The vials were sparged with argon for an additional 10–15 seconds and then sealed with a screw cap under a stream of argon. The vials were subsequently irradiated with blue LED light for 4 h in a Hepatochem device. Following this time, each of the vials was removed from the Hepatochem device. A 1:1 mixture of a saturated aqueous solution of NaCl and H_2O (1.5 mL) was added to each vial and then each reaction was extracted with Et_2O (3 x 3 mL). Each of the combined organic extracts was dried over $MgSO_4$, filtered, and concentrated under rotary evaporation in a rotavap water bath at 27 °C (at a pressure of ~60–100 mmHg for volatile products). NMR yields were determined using quantitative ^{1}H NMR spectroscopy with pyrazine as an added standard. The ^{1}H NMR data for the tertiary bromide **11a** was consistent with those reported in the literature.[8]

General Procedure #5 (substrate scope): A 20 mL scintillation vial containing a stir bar was successively charged with cesium oxalate (1 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.01 equiv), cesium carbonate (0.5 equiv), CH_2Cl_2 (1.5 mL) that was degassed by sparging with a balloon of argon for 15 min, and diethyl bromomalonate (1.5 equiv) were added. The vial was sparged with argon for an additional 10–15 seconds and then sealed with a screw cap under a stream of argon. The vial was placed in a Hepatochem device and irradiated with blue LED light. Tertiary alcohol-derived cesium oxalates were irradiated for 4 h and secondary alcohol-derived cesium oxalates were irradiated for 24 h. The vial was subsequently removed from the Hepatochem device and transferred to a separatory funnel with a 1:1 mixture of a saturated aqueous solution of NaCl and H_2O (1.5 mL) and then extracted with Et_2O (3 x 3 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under rotary evaporation in a rotavap water bath at 27 °C (at a pressure of ~60–100 mmHg for volatile products). The crude residue was purified by silica gel chromatography to afford the brominated products. To mitigate elimination of tertiary bromides to the corresponding alkenes during purification, silica gel columns were treated with Et_3N as needed (see below).

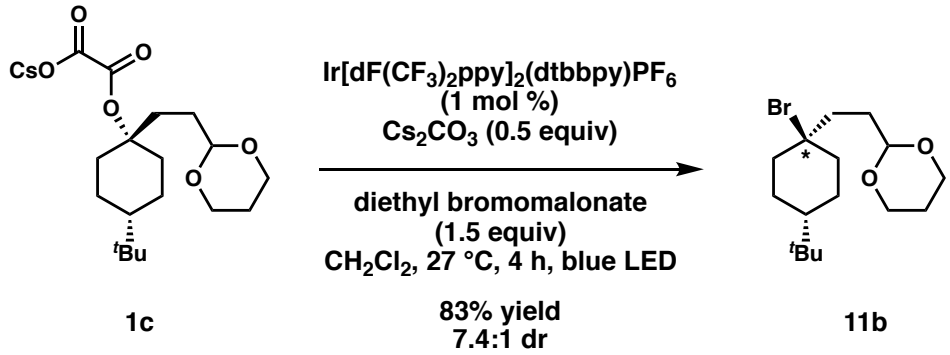
Bromides **11a** and **11b** were contaminated with diethyl bromomalonate and diethyl malonate following purification by column chromatography. For these products, the diethyl bromomalonate and diethyl malonate were removed by dissolving in THF (0.9 mL) and MeOH (0.45 mL), cooling to 0 ºC, and then adding a 3 M aqueous solution of NaOH (0.3 mL) dropwise. After stirring at 0 ºC for 5 min and room temperature for 25 min, the solution was diluted with H_2O (1 mL) and extracted with Et_2O (4 x 2 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford the bromide products.



83% yield

(3-bromo-3-methylbutyl)benzene (11a): Prepared according to general procedure #5 using cesium oxalate **1a** (111 mg, 0.30 mmol). A silica gel column was eluted with two column volumes of 3% Et_3N/2% Et_2O/pentane. The crude material was then purified using this column (isocratic: 2% Et_2O/pentane). Residual diethyl bromomalonate and diethylmalonate were removed by treatment with aqueous NaOH according to general procedure #5 to deliver bromide **11a** as a pale yellow oil (57 mg, 83% yield). The ^1H NMR data for tertiary bromide **11a** was consistent with those reported in the literature.[8]

TLC R_f = 0.37 (hexanes, *p*-anisaldehyde).



2-(2-((1*r*,4*r*)-1-bromo-4-(*tert*-butyl)cyclohexyl)ethyl)-1,3-dioxane (11b): Prepared according to general procedure #5 using cesium oxalate **1c** (128 mg, 0.27 mmol). A silica gel column was eluted with two column volumes of 3% Et_3N/5% Et_2O/pentane. The crude material was then purified using this column (isocratic: 2% Et_2O/pentane). Residual diethyl bromomalonate and diethylmalonate were removed by treatment with aqueous NaOH according to general procedure #5 to afford bromide **11b** as a mixture of inseparable diastereomers as a clear colorless oil (75 mg, 83% yield, 7.4:1 dr).

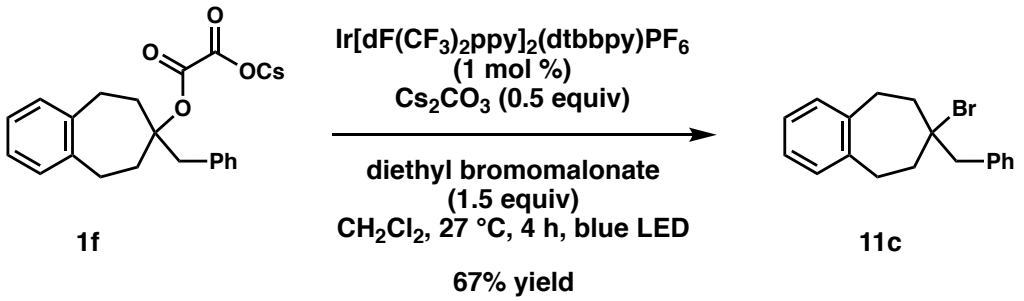
TLC R_f = 0.28 (10% Et_2O/hexanes, *p*-anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (t, *J* = 4.2 Hz, 1H), 4.10 (ddt, *J* = 10.4, 5.0, 1.4 Hz, 2H), 3.76 (dddd, *J* = 11.9, 10.4, 2.6, 1.6 Hz, 2H), 2.18 – 2.08 (m, 2H), 2.08 – 2.00 (m, 1H), 1.98 – 1.85 (m, 4H), 1.73 – 1.47 (m, 4H), 1.40 – 1.27 (m, 3H), 0.95 (tt, *J* = 11.9, 3.6 Hz, 1H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 102.3, 76.6, 67.1, 47.6, 41.5, 41.4, 32.6, 31.2, 27.6, 25.9, 23.9.

FTIR (NaCl, thin film, cm^{-1}): 2948, 2849, 2729, 2657, 1446, 1366, 1286, 1248, 1147, 1079, 1040, 1009, 974.

HRMS (FAB+, *m/z*): calc'd for $C_{16}H_{28}BrO_2$ $(M+H-H_2)^+$: 331.1273, found: 331.1251.



7-benzyl-7-bromo-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (11c): Prepared according to general procedure #5 using cesium oxalate **1f** (136 mg, 0.30 mmol). A silica gel column was eluted with two column volumes of 2% Et_3N/pentane. The crude material was then purified using this column (isocratic: 2% Et_2O/pentane) to provide bromide **11c** as a viscous clear colorless oil (63

mg, 67% yield).

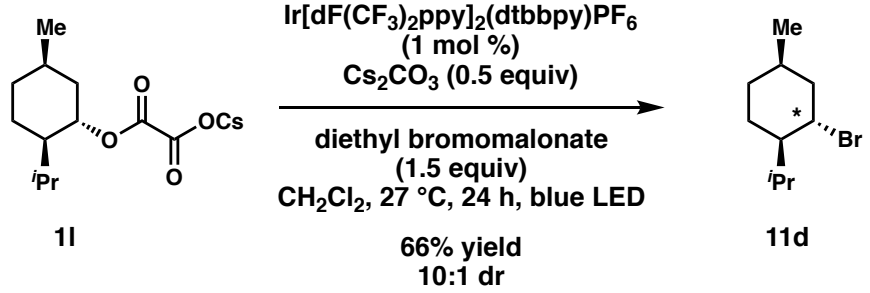
TLC R_f = 0.33 (3% Et_2O/pentane, *p*-anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 5H), 7.09 (s, 4H), 3.46 – 3.31 (m, 2H), 3.29 (s, 2H), 2.66 (dd, *J* = 14.9, 7.1 Hz, 2H), 2.33 (dddd, *J* = 14.9, 7.4, 2.3, 1.4 Hz, 2H), 1.83 – 1.56 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 136.4, 131.5, 129.1, 128.0, 127.1, 126.5, 80.3, 54.2, 41.9, 32.6.

FTIR (NaCl, thin film, cm^{-1}): 3017, 2946, 1604, 1494, 1453, 1270, 1077, 1034, 936.

HRMS (EI, *m/z*): calc'd for $C_{18}H_{18}Br$ $(M+H-H_2)^+$: 313.0592, found: 313.0606.



(1*R*,2*S*,4*R*)-2-bromo-1-isopropyl-4-methylcyclohexane (11d): Prepared according to general procedure #5 using cesium oxalate **1l** (110 mg, 0.31 mmol). The crude residue was purified by silica gel chromatography (isocratic: 1% Et_2O/pentane) to give bromide **11d** as a clear colorless oil (44.1 mg, 66% yield, 10:1 dr).

TLC R_f = 0.66 (pentane, *p*-anisaldehyde).

$[\alpha]_D^{25}$ = +36.2° (c = 1.00, $CHCl_3$).

^{1}H NMR (major diastereomer, 400 MHz, $CDCl_3$) δ 4.51 (tt, *J* = 7.2, 3.2 Hz, 1H), 2.11 – 1.94 (m, 3H), 1.88 (ddt, *J* = 11.3, 7.6, 5.1 Hz, 1H), 1.81 – 1.72 (m, 1rH), 1.60 – 1.40 (m, 3H), 1.38 – 1.23 (m, 1H), 0.93 (dd, *J* = 6.8, 2.3 Hz, 6H), 0.85 (d, *J* = 6.7 Hz, 3H).

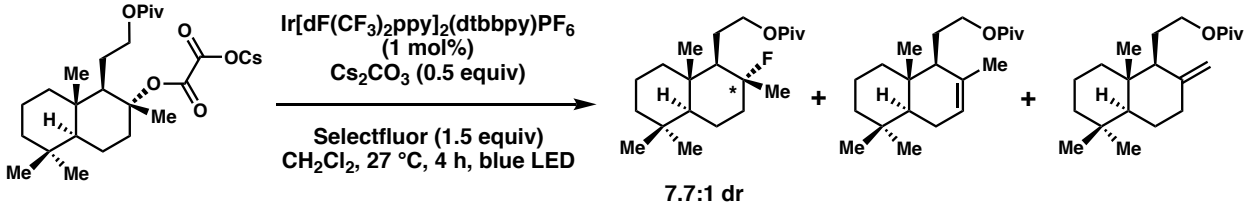
^{13}C NMR (major diastereomer, 101 MHz, $CDCl_3$) δ 57.4, 50.2, 41.9, 30.4, 28.9, 28.5, 21.2, 21.1, 19.8, 18.3.

FTIR (NaCl, thin film, cm^{-1}): 2959, 1458, 1386, 1190, 1020, 974.

HRMS (GC-EI, *m/z*): calc'd for $C_{10}H_{18}Br$ $(M-H)^+$: 217.0592, found: 217.0562.

8. Deoxyfluorination Reactions

General Procedure #6: In a nitrogen-filled glovebox, a 20 mL scintillation vial was charged with Selectfluor (1.5 equiv) and Cs_2CO_3 (0.5 equiv). The vial was sealed with a screw cap and removed from the glovebox. A stir bar was then added, followed by cesium oxalate (1.0 equiv) and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.01 equiv). The vial was layered with argon for 45 seconds and CH_2Cl_2 (1.5 mL) was added (degassed by sparging with a balloon of argon for 20 min). The vial was sparged with argon for an additional 10–15 seconds and then sealed with a screw cap. The vial was placed in a Hepatochem device and irradiated with blue LED light. Tertiary alcohol-derived cesium oxalates were irradiated for 4 h and secondary alcohol-derived cesium oxalates were irradiated for 24 h. Following this time, the reaction was removed from the Hepatochem device. The solid was removed by filtering through a pipette plug and rinsing with CH_2Cl_2 (15 mL), and the solvent was removed under rotary evaporation. For volatile fluoride **12d**, the reaction was performed in CD_2Cl_2 and a crude yield obtained directly using ^{1}H NMR and pyrazine as an internal standard (no evaporation of solvent was performed). The crude residues were then purified by silica gel chromatography to afford the fluorinated products. To mitigate elimination of tertiary fluorides to the corresponding alkenes during purification, silica gel columns were pre-eluted with Et_3N-containing solvent as needed for selected products (see below).



2-((1*R*,4a*S*,8a*S*)-2-fluoro-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)ethyl pivalate (12a):

Prepared according to general procedure #6 using cesium oxalate **1e** (163 mg, 0.30 mmol).[2] A silica gel column was pre-eluted with two column volumes of 3% Et_3N/pentane, followed by two column volumes of pentane. Purification of the crude residue was then performed on this column (isocratic: 2% Et_2O/pentane) to afford a 89:2:9 mixture of **12a** (7.7:1 dr), **SI-24**, and **SI-25** in (51 mg, 50% yield: 45% **12a**, 1% **SI-24**, 4% **SI-25**).

TLC R_f = 0.37 (5% Et_2O/pentane, *p*-anisaldehyde).

$[\alpha]_D^{25}$ = +9.9° (c = 1.0, $CHCl_3$).

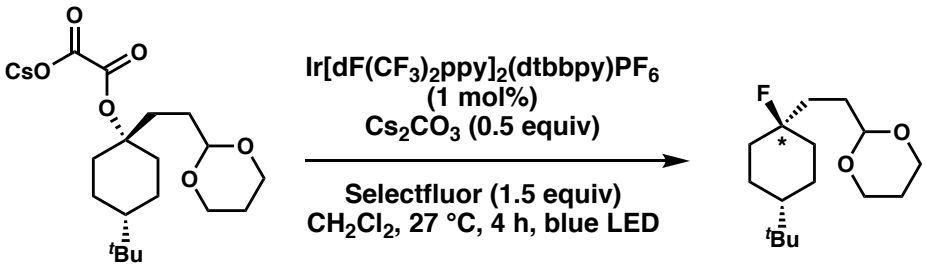
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 – 4.03 (m, 2H), 1.98 (ddd, *J* = 12.3, 4.1, 3.0 Hz, 1H), 1.76 – 1.50 (m, 6H), 1.51 – 1.36 (m, 3H), 1.34 (dd, *J* = 24.1, 1.1 Hz, 3H), 1.27 – 1.20 (m, 1H), 1.19 (s, 9H), 1.16 – 1.06 (m, 1H), 1.04 – 0.89 (m, 2H), 0.88 (s, 3H), 0.78 (s, 3H), 0.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 98.5 (d, *J* = 166.5 Hz), 65.6 (d, *J* = 5.2 Hz), 55.8 (d, *J* = 1.9 Hz), 55.4 (d, *J* = 17.4 Hz), 41.9, 41.1 (d, *J* = 20.7 Hz), 39.6, 38.8, 38.7 (d, *J* = 10.8 Hz), 33.5, 33.4, 27.4, 24.4, 22.5 (d, *J* = 26.6 Hz), 21.6, 20.4 (d, *J* = 11.7 Hz), 18.5, 15.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ *major diastereomer:* -118.24 (qt, *J* = 24.2, 14.8 Hz), *minor diastereomer:* -156.64 – -157.46 (m).

FTIR (NaCl, thin film, cm^{-1}): 2955, 2870, 1728, 1459, 1284, 1157.

HRMS (ESI+, *m/z*): calc'd for $C_{21}H_{37}FO_2$ $(M+Na)^+$: 363.2675, found: 363.2678.



1c **59% yield** **3:1 dr** **12b**

2-(2-((1*r*,4*r*)-4-(*tert*-butyl)-1-fluorocyclohexyl)ethyl)-1,3-dioxane (12b):

Prepared according to general procedure #6 using cesium oxalate **1c** (142 mg, 0.30 mmol). A silica gel column was pre-eluted with two column volumes of 3% Et_3N/pentane, followed by two column volumes of pentane. Purification of the crude residue was then performed on this column (0–10% Et_2O/pentane) to afford fluoride **12b** as a clear oil (48.5 mg, 59% yield, 3:1 dr).

TLC R_f (major diastereomer) = 0.48 (10% Et_2O/pentane, *p*-anisaldehyde).

TLC R_f (minor diastereomer) = 0.55 (90:20 pentane/Et_2O, *p*-anisaldehyde).

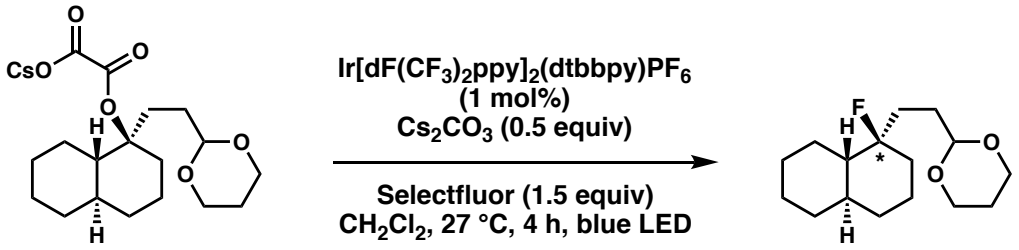
^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer:* δ 4.52 (t, *J* = 4.8 Hz, 1H), 4.15 – 4.05 (m, 2H), 3.81 – 3.70 (m, 2H), 2.15 – 2.00 (m, 1H), 1.98 – 1.86 (m, 2H), 1.83 – 1.64 (m, 4H), 1.65 – 1.52 (m, 2H), 1.40 – 1.28 (m, 3H), 1.27 – 1.17 (m, 1H), 1.07 – 0.90 (m, 2fH), 0.85 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) *major diastereomer:* δ 102.5, 94.9 (d, *J* = 169.9 Hz), 67.1, 47.5, 36.1 (d, *J* = 20.3 Hz), 35.5 (d, *J* = 22.8 Hz), 35.1 (d, *J* = 23.2 Hz), 32.6, 29.0 (d, *J* = 4.7 Hz), 27.7, 26.0, 24.7 (d, *J* = 11.9 Hz), 22.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ *minor diastereomer:* –138.26 (tt, *J* = 24.9, 12.8 Hz), *major diastereomer:* -161.48 – -162.22 (m).

FTIR (NaCl, thin film, cm^{-1}): 2949, 2848, 1469, 1366, 1240, 1148, 1007, 926.

HRMS (FAB+, *m/z*): calc'd for $C_{16}H_{29}FO_2$ $(M+H–H_2)^–$: 271.2073, found: 271.2084.



2-(2-((4a*R*,8a*S*)-1-fluorodecahydronaphthalen-1-yl)ethyl)-1,3-dioxane (12c):

Prepared according to general procedure #6 using cesium oxalate **1d** (142 mg, 0.30 mmol). A silica gel column (20 g) was pre-eluted with two column volumes of 3% Et_3N/pentane, followed by two column volumes of 2% Et_2O/pentane. The crude material was dry-loaded onto 400 mg celite, then purified using this column (2–10% Et_2O/pentane) to afford a diastereomeric mixture of fluoride **12c** as a clear oil (26 mg, 32% yield, 1.25:1 dr).

TLC R_f = 0.43 (20% Et_2O/pentane, *p*-anisaldehyde).

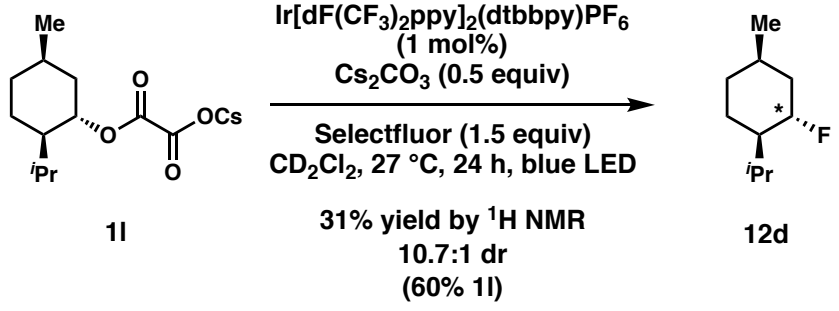
^{1}H NMR (400 MHz, $CDCl_3$): *Note: mixture of diastereomers*: δ 4.57 – 4.50 (m, 1H), 4.50 (t, *J* = 5.0 Hz, 1H), 4.15 – 4.05 (m, 4H), 3.81 – 3.68 (m, 4H), 2.15 – 1.99 (m, 3H), 1.90 – 1.49 (m, 23H), 1.46 – 1.26 (m, 6H), 1.26 – 1.05 (m, 7H), 1.02 – 0.85 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): *Note: mixture of diastereomers*: δ 102.7, 102.5, 98.6 (d, *J* = 172.4 Hz), 97.1 (d, *J* = 172.4 Hz), 67.1, 52.0 (d, *J* = 19.0 Hz), 47.8 (d, *J* = 21.1 Hz), [aliphatic region: 39.6, 39.5, 37.4, 35.0, 35.0, 34.8, 34.8, 34.68, 34.67, 33.80, 33.78, 33.76, 31.7, 31.4, 30.5, 29.9, 29.8, 28.78, 28.75, 26.8, 26.5, 26.4, 26.2, 26.0, 25.9, 25.2, 25.2, 24.9, 24.83, 24.81, 24.7, 22.8, 22.6, 21.28, 21.26].

^{19}F NMR (376 MHz, $CDCl_3$) δ -146.05 – -146.60 (m), -166.95 (tdd, *J* = 39.5, 19.5, 8.3 Hz).

FTIR (NaCl, thin film, cm^{-1}): 2928, 2851, 1449, 1376, 1146, 1002, 934.

HRMS (FAB+, *m/z*): calc'd for $C_{16}H_{27}FO_2$ $(M+\cdot - H)^-$: 269.1917, found: 269.1918.



(1*R*,2*S*,4*R*)-2-fluoro-1-isopropyl-4-methylcyclohexane (12d):

Prepared according to general procedure #6 using cesium oxalate **1l** (108 mg, 0.30 mmol)[2] and CD_2Cl_2 as a solvent. Fluoride **12d** was formed in 31% yield (with 60% oxalate **1l** remaining),

which was determined by ^{1}H NMR with pyrazine as an internal standard. For characterization, the crude material in CD_2Cl_2 was loaded onto a silica gel column and purified using pentane (isocratic) to afford fluoride **12d** as a clear oil (4 mg, 8% yield, 10.7:1 dr).

TLC R_f = 0.65 (2% Et_2O/pentane, *p*-anisaldehyde).

$[\alpha]_D^{25}$ = +17.4° (c = 0.20, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (dtd, *J* = 47.8, 6.9, 3.3 Hz, 1H), 1.97 (dtd, *J* = 8.4, 4.8, 3.9, 2.6 Hz, 1H), 1.83 (dq, *J* = 13.5, 6.7 Hz, 1H), 1.78 – 1.67 (m, 1H), 1.66 – 1.48 (m, 2H), 1.49 – 1.36 (m, 3H), 1.29 – 1.16 (m, 1H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.91 – 0.88 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 91.5 (d, *J* = 167.8 Hz), 47.0 (d, *J* = 16.8 Hz), 37.0 (d, *J* = 19.3 Hz), 30.0 (d, *J* = 1.4 Hz), 27.7 (d, *J* = 6.8 Hz), 26.5 (d, *J* = 6.6 Hz), 20.9, 20.7 (d, *J* = 5.1 Hz), 20.5, 19.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -179.53 – -179.86 (m).

FTIR (NaCl, thin film, cm^{-1}): 2928, 2872, 1460, 1369, 1261, 1028.

HRMS (EI+, *m/z*): calc'd for $C_{10}H_{19}F$ $(M+\cdot)^+$: 158.1471, found: 158.1445.

9. References

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6. (–)-Thujol was prepared from (–)-α-thujone (70%, purchased from SigmaAldrich 89230) according to the following literature procedure, where L-selectride (2.0 equiv) was substituted for other reported reductants such as $NaBH_4$: Banthorpe, D. V.; Davies, H. ff. S. *J. Chem. Soc.* **1968**, *B*, 1356. All recorded characterization data matched the literature reports (for NMR data for both (–)-thujol and its diastereomer (–)-neothujol see: Reinhardt, N.; Fischer, J.; Coppi, R.; Blum, E.; Brandt, W.; Dräger, B. *Bioorg. Chem.* **2014**, *53*, 37–49).
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Parameter	Value
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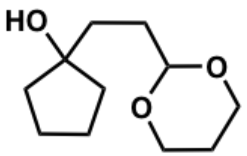
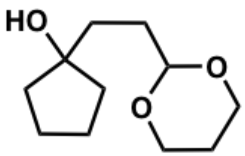
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-04-25T10:12:08
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



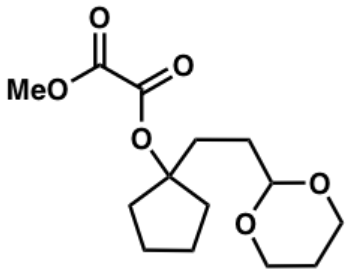
SI-2

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-295-1/ 3/ fid
Title	DCG-5-295-1.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-04-25T10:41:33
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



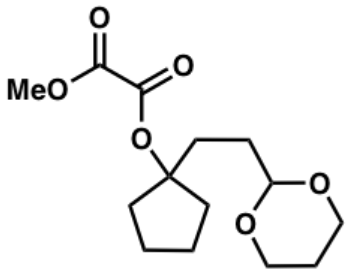
SI-2

Parameter	Value
Data File Name	JYS-2-136-F1-cyclopentyl-acetal-Me-oxalate/ fid
Title	JYS-2-136-F1
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Acquisition Date	2018-04-18T18:55:19
Spectrometer	499.64



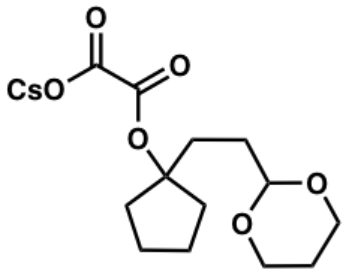
SI-3

Parameter	Value
Data File Name	JYS-2-136-F1-cyclopentyl-acetal-Me-oxalate/ fid
Title	JYS-2-136-F1
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Acquisition Date	2018-04-18T18:56:39
Spectrometer Frequency	125.65
Spectral Width	31446.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



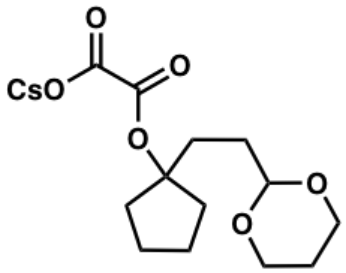
SI-3

Parameter	Value
Data File Name	JYS-2-181-cyclopentyl-acetal-cs-ox/ 1/ fid
Title	JYS-2-181-cyclopentyl-acetal-cs-ox.1.fid
Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	295.1
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-05-02T07:18:52
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



1b

Parameter	Value
Data File Name	JYS-2-181-cyclopentyl-acetal-cs-ox/ 2/ fid
Title	JYS-2-181-cyclopentyl-acetal-cs-ox.2.fid
Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	295.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	64.2
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-05-02T07:34:53
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



1b

Parameter	Value
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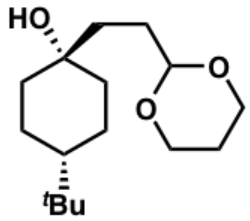
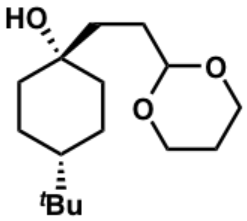
Title	PROTON01
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	22
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Acquisition Date	2018-04-17T00:12:04
Spectrometer Frequency	499.64
Spectral Width	8000.0
Nucleus	1H
Acquired Size	24000
Spectral Size	65536



SI-4

Parameter	Value
Data File Name	JYS-2-130-F1-tbu-cyclohexyl-acetal-maj-diast/ CARBON01.fid/ fid
Title	CARBON01
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Acquisition Date	2018-04-17T00:13:25
Spectrometer Frequency	125.65
Spectral Width	31446.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



SI-4

Parameter	Value
Data File Name	JYS-2-130-F3-cyclohexyl-acetal-alcohol-minor-diast/ PROTON01.fid/ fid
Title	PROTON01
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
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Spectral Width	8000.0
Nucleus	1H
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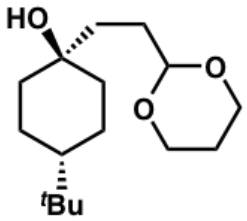

SI-5

Parameter	Value
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Title	CARBON01
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
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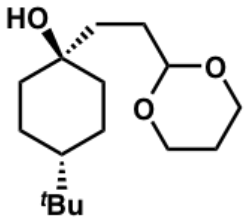
Spectral Width	31446.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



SI-5

Parameter	Value
Data File Name	JYS-2-161-F1-tbu-cyclohexanol-acetal-Me-ox-maj-diast/ 1/ fid
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Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
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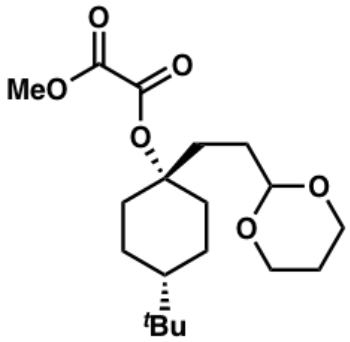
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



SI-6

Parameter	Value
Data File Name	JYS-2-161-F1-tbu-cyclohexanol-acetal-Me-ox-maj-diast/ 2/ fid
Title	JYS-2-161-F1-tbu-cyclohexanol-acetal-Me-ox-maj-diast.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
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Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
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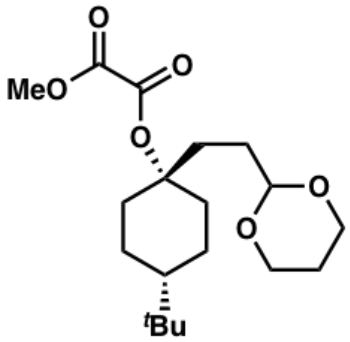
Spectral Size	65536



SI-6

Parameter	Value
Data File Name	JYS-2-166-tbucyclohexyl-acetal-cs-ox-majdiast-cd3od/ 1/ fid
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Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	295.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	98.9
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
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Nucleus	1H
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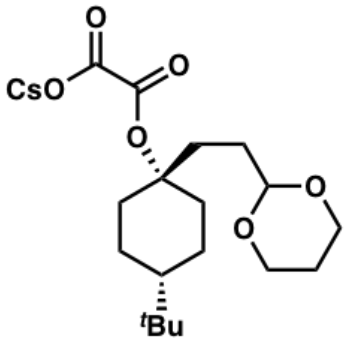
Spectral Size	65536



1c

Parameter	Value
Data File Name	JYS-2-166-tbucyclohexyl-acetal-cs-ox-majdiast-cd3od/ 2/ fid
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Pulse Width	10.0000
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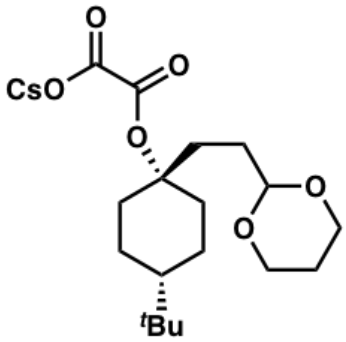
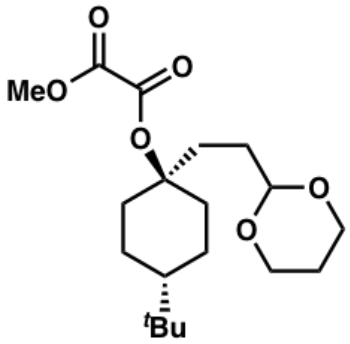
Spectral Size	65536



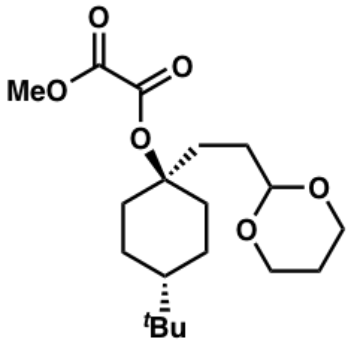
1c

Parameter	Value
Data File Name	JYS-2-162-F1-tbu-cyclohexanol-acetal-Me-ox-min-diast/ 1/ fid
Title	JYS-2-162-F1-tbu-cyclohexanol-acetal-Me-ox-min-diast.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-04-21T14:28:30
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



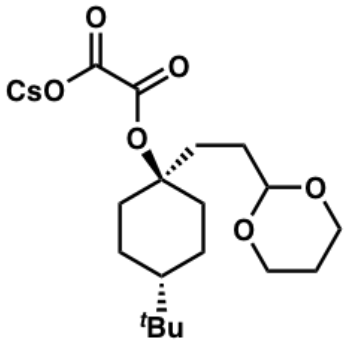
SI-7

Parameter	Value
Data File Name	JYS-2-162-F1-tbu-cyclohexanol-acetal-Me-ox-min-diast/ 2/ fid
Title	JYS-2-162-F1-tbu-cyclohexanol-acetal-Me-ox-min-diast.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-04-21T14:58:15
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



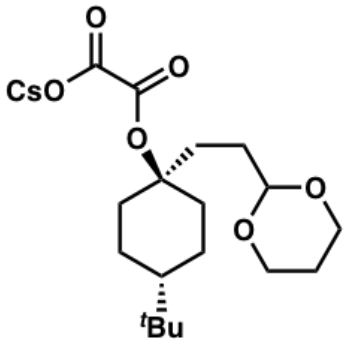
SI-7

Parameter	Value
Data File Name	JYS-2-167-tbucyclohexyl-acetal-cs-ox-mindiast-cd3od/ 1/ fid
Title	JYS-2-167-tbucyclohexyl-acetal-cs-ox-mindiast-cd3od.1.fid
Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	295.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	112.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-04-24T15:59:01
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



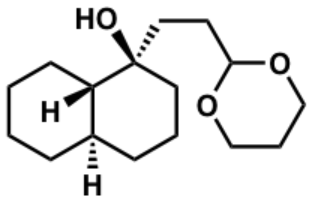
1c'

Parameter	Value
Data File Name	JYS-2-167-tbucyclohexyl-acetal-cs-ox-mindiast-cd3od/ 2/ fid
Title	JYS-2-167-tbucyclohexyl-acetal-cs-ox-mindiast-cd3od.2.fid
Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	295.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	50.3
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-04-24T16:14:12
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



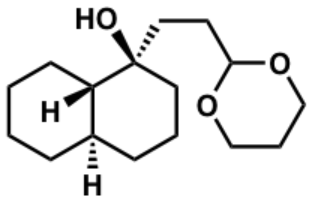
1c'

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-272-1/ 1/ fid
Title	DCG-5-272-1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-04-02T23:40:19
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



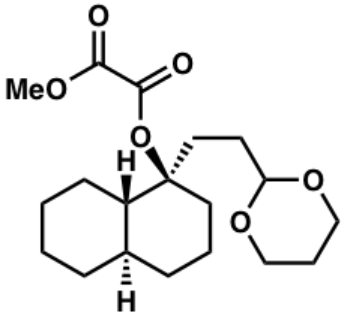
SI-8

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-272-1/ 3/ fid
Title	DCG-5-272-1.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	128
Receiver Gain	50.3
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-04-03T00:00:42
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



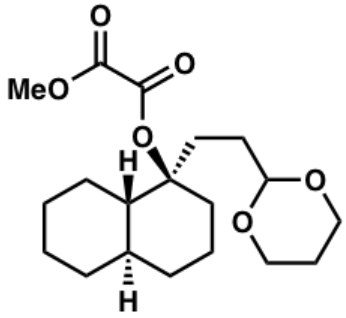
SI-8

Parameter	Value
Data File Name	JYS-2-144-F1-decalin-acetal-Me-oxalate/ PROTON01.fid/ fid
Title	PROTON01
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	26
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Acquisition Date	2018-04-18T21:46:47
Spectrometer Frequency	499.64
Spectral Width	8000.0
Nucleus	1H
Acquired Size	24000
Spectral Size	65536



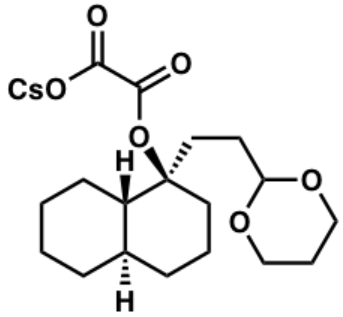
SI-9

Parameter	Value
Data File Name	JYS-2-144-F1-decalin-acetal-Me-oxalate/ CARBON01.fid/ fid
Title	CARBON01
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Acquisition Date	2018-04-18T21:48:08
Spectrometer Frequency	125.65
Spectral Width	31446.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



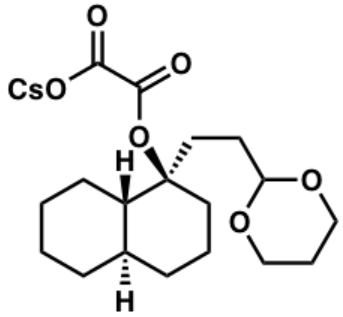
SI-9

Parameter	Value
Data File Name	JYS-2-165-clean-decalin-acetal-cs-ox/ 1/ fid
Title	JYS-2-165-clean-decalin-acetal-cs-ox.1.fid
Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	295.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	98.9
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-05-01T05:32:07
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



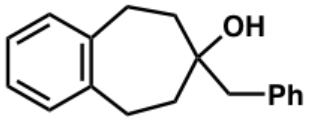
1d

Parameter	Value
Data File Name	JYS-2-165-clean-decalin-acetal-cs-ox/ 2/ fid
Title	JYS-2-165-clean-decalin-acetal-cs-ox.2.fid
Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	295.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	55.5
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-05-01T05:47:50
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



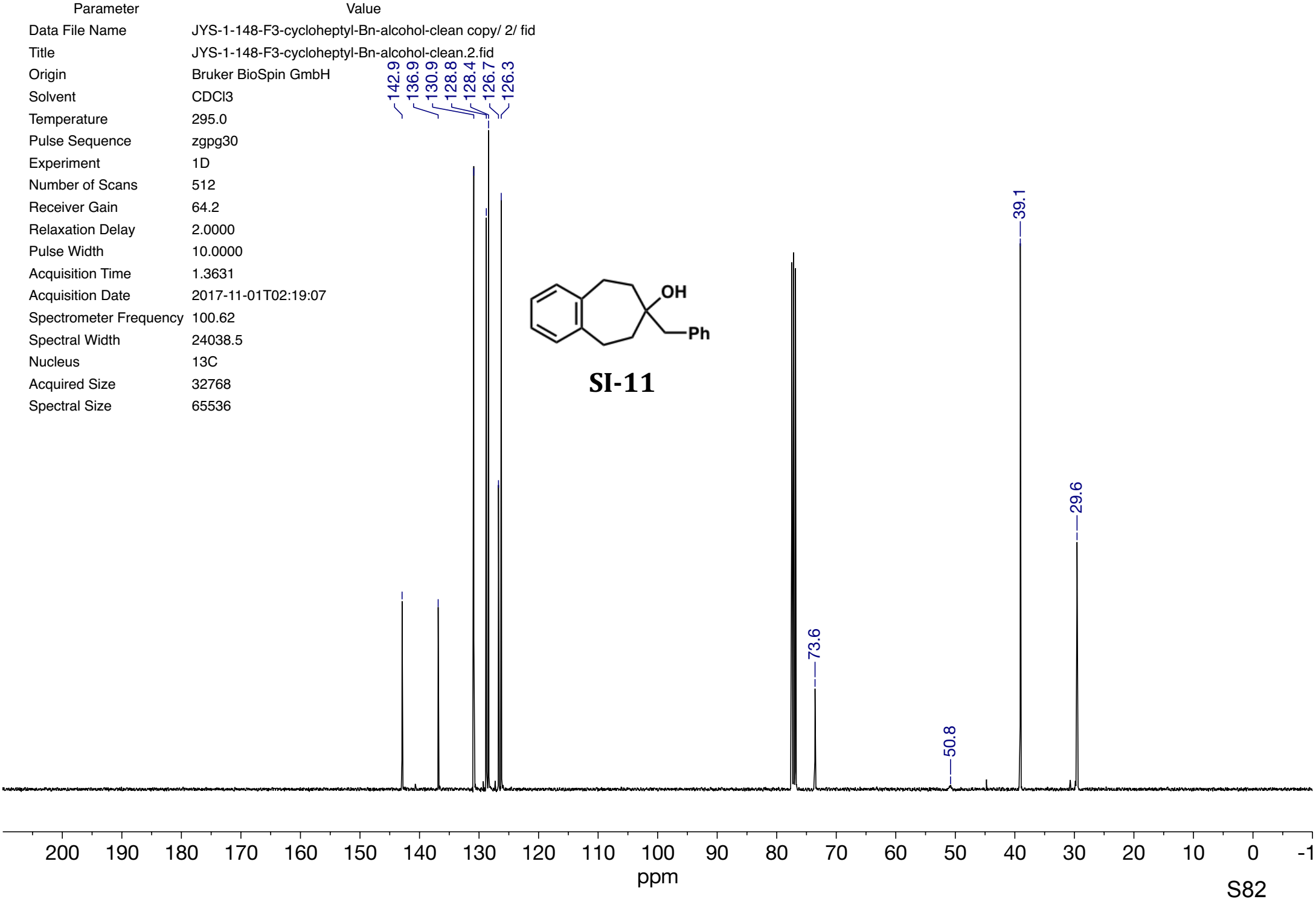
1d

Parameter	Value
Data File Name	JYS-1-148-F3-cycloheptyl-Bn-alcohol-clean copy/ 1/ fid
Title	JYS-1-148-F3-cycloheptyl-Bn-alcohol-clean.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-01T01:49:23
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



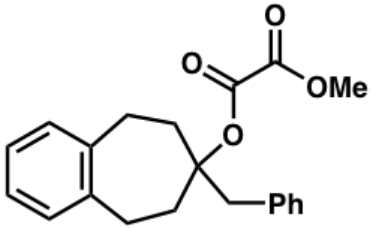
SI-11

Parameter	Value
Data File Name	JYS-1-148-F3-cycloheptyl-Bn-alcohol-clean copy/ 2/ fid
Title	JYS-1-148-F3-cycloheptyl-Bn-alcohol-clean.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-01T02:19:07
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



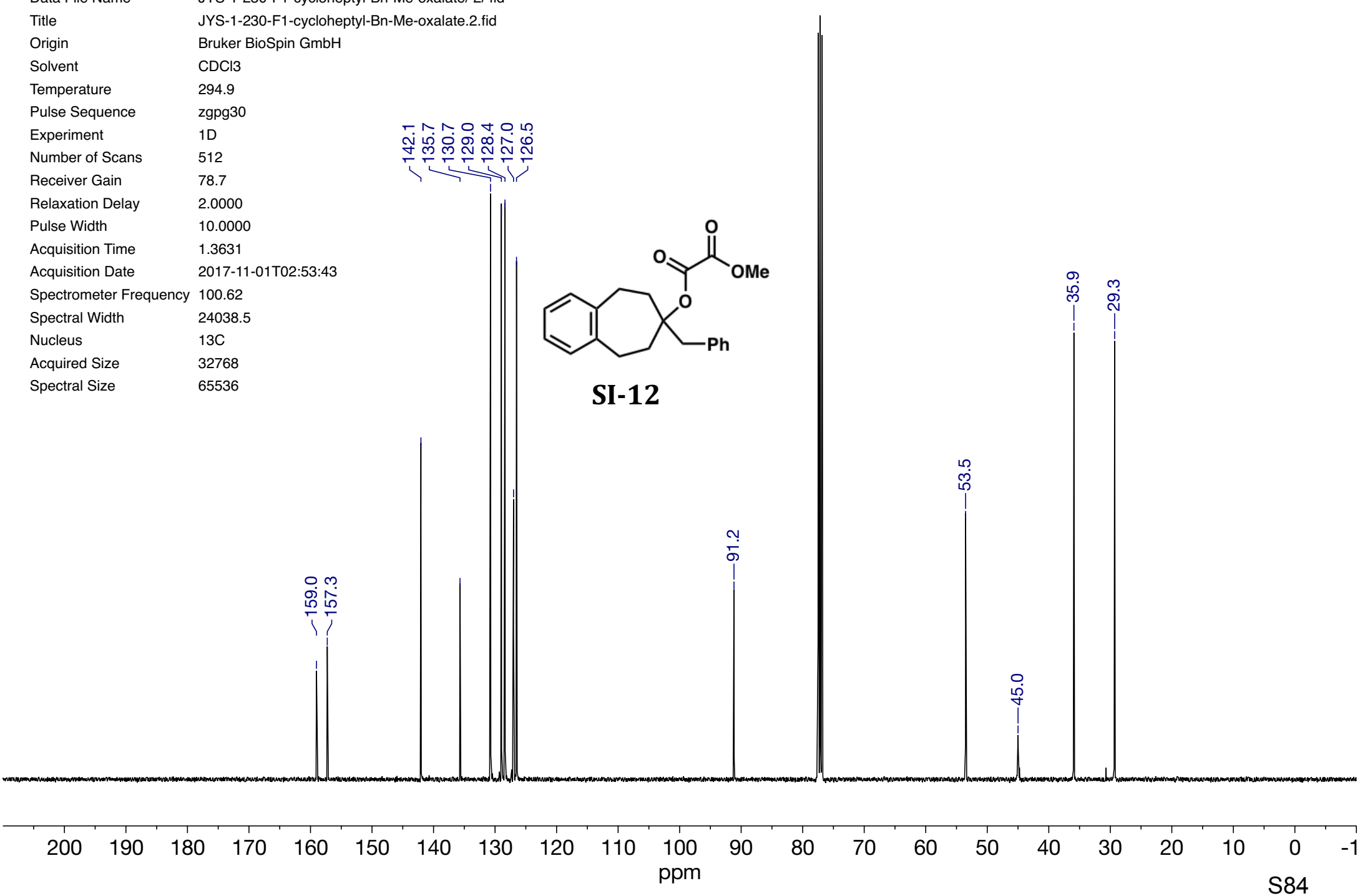
SI-11

Parameter	Value
Data File Name	JYS-1-230-F1-cycloheptyl-Bn-Me-oxalate/ 1/ fid
Title	JYS-1-230-F1-cycloheptyl-Bn-Me-oxalate.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-01T02:23:58
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



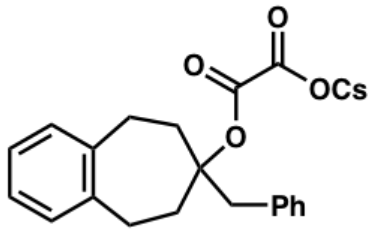
SI-12

Parameter	Value
Data File Name	JYS-1-230-F1-cycloheptyl-Bn-Me-oxalate/ 2/ fid
Title	JYS-1-230-F1-cycloheptyl-Bn-Me-oxalate.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-01T02:53:43
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



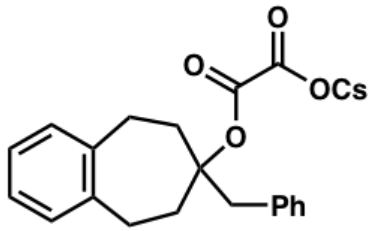
SI-12

Parameter	Value
Data File Name	JYS-1-261-cycloheptyl-Bn-Cs-oxalate/ 4/ fid
Title	JYS-1-261-cycloheptyl-Bn-Cs-oxalate.4.fid
Origin	Bruker BioSpin GmbH
Solvent	DMSO
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	176.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-08T20:05:06
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



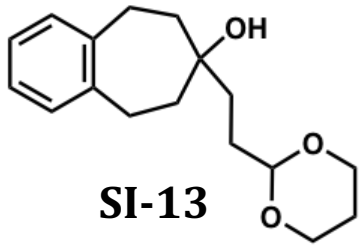
1f

Parameter	Value
Data File Name	JYS-1-261-cycloheptyl-Bn-Cs-oxalate/ 2/ fid
Title	JYS-1-261-cycloheptyl-Bn-Cs-oxalate.2.fid
Origin	Bruker BioSpin GmbH
Solvent	DMSO
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-07T00:22:55
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



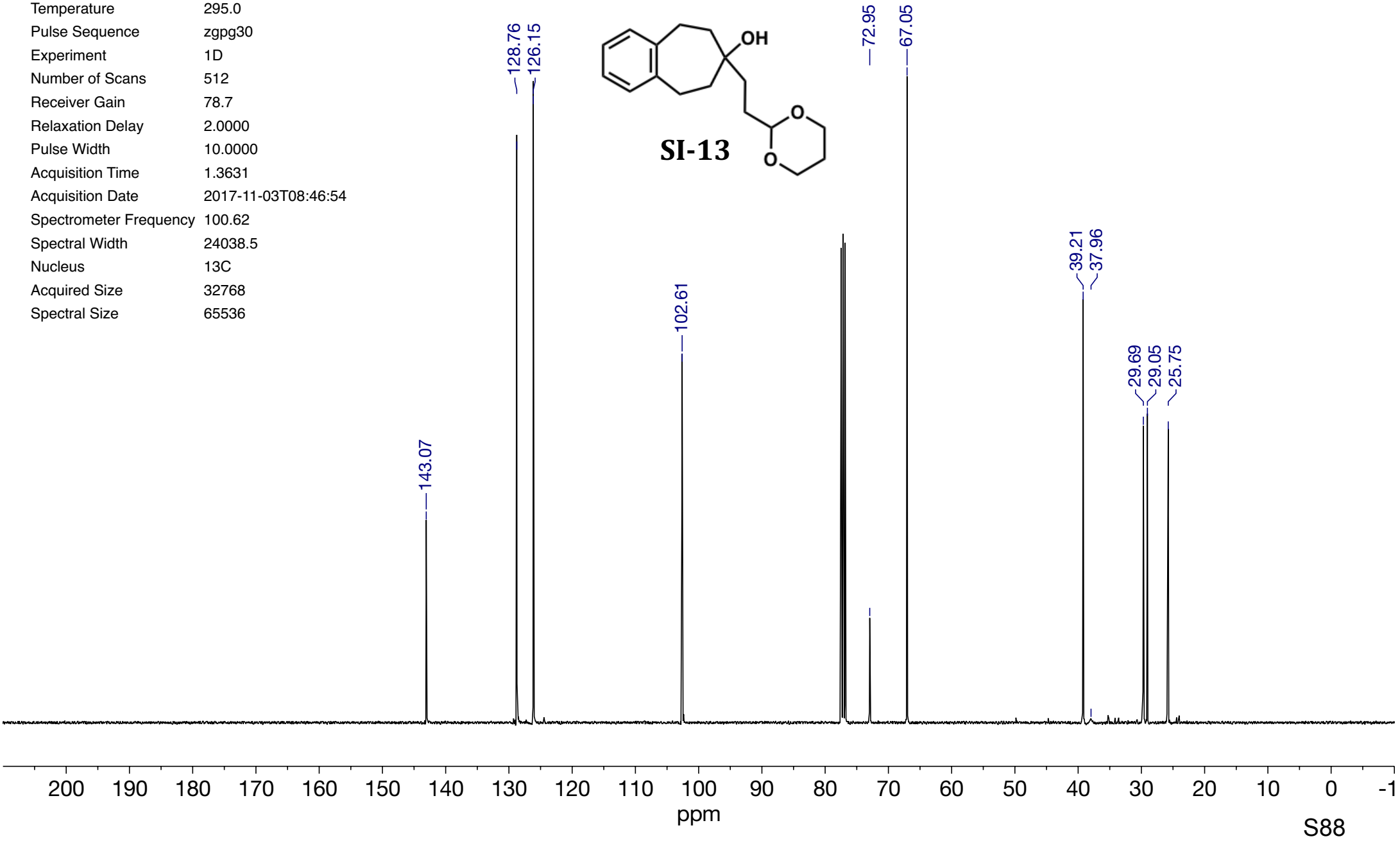
1f

Parameter	Value
Data File Name	JYS-1-185-F3-cycloheptyl-acetal-alcohol/ 1/ fid
Title	JYS-1-185-F3-cycloheptyl-acetal-alcohol.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-03T08:17:10
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

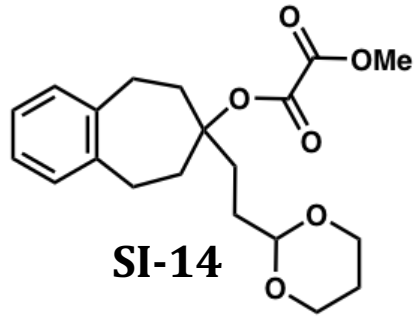


SI-13

Parameter	Value
Data File Name	JYS-1-185-F3-cycloheptyl-acetal-alcohol/ 2/ fid
Title	JYS-1-185-F3-cycloheptyl-acetal-alcohol.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-03T08:46:54
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

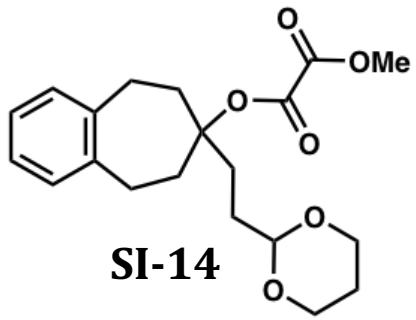


Parameter	Value
Data File Name	JYS-1-187-B-F1-cycloheptyl-acetal-Me-oxalate/ 1/ fid
Title	JYS-1-187-B-F1-cycloheptyl-acetal-Me-oxalate.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-03T08:51:17
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



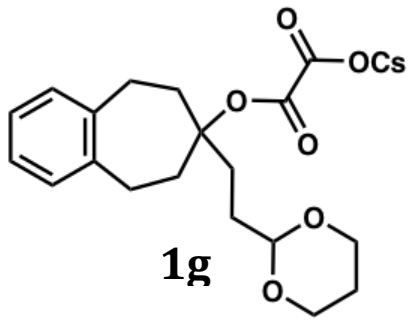
SI-14

Parameter	Value
Data File Name	JYS-1-187-B-F1-cycloheptyl-acetal-Me-oxalate/ 2/ fid
Title	JYS-1-187-B-F1-cycloheptyl-acetal-Me-oxalate.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-03T09:21:05
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



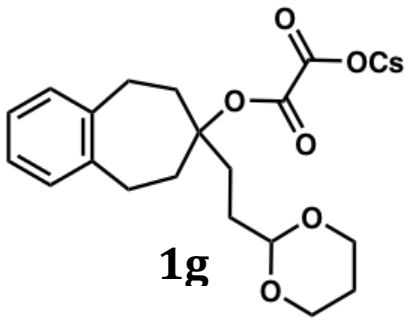
SI-14

Parameter	Value
Data File Name	JYS-1-196-cycloheptyl-acetal-Cs-oxalate/ 1/ fid
Title	JYS-1-196-cycloheptyl-acetal-Cs-oxalate.1.fid
Origin	Bruker BioSpin GmbH
Solvent	D2O
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	112.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-03T09:27:25
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

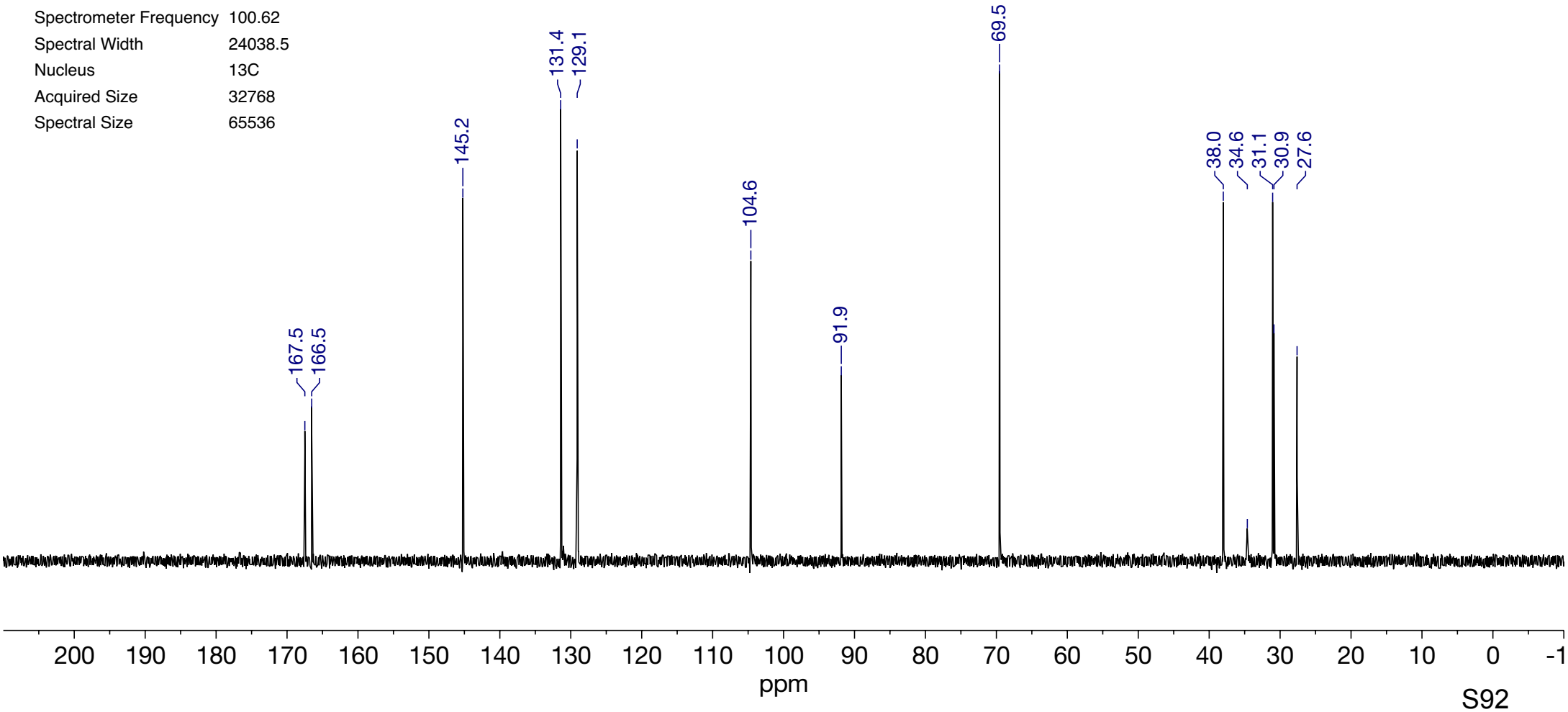


1g

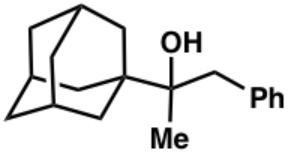
Parameter	Value
Data File Name	JYS-1-196-cycloheptyl-acetal-Cs-oxalate/ 2/ fid
Title	JYS-1-196-cycloheptyl-acetal-Cs-oxalate.2.fid
Origin	Bruker BioSpin GmbH
Solvent	D2O
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-03T09:57:47
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



1g

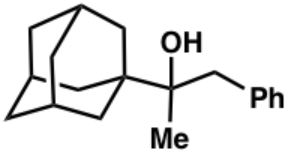


Parameter	Value
Data File Name	JYS-1-120-F1-adamantyl-bn-alcohol-clean/ 1/ fid
Title	JYS-1-120-F1-adamantyl-bn-alcohol-clean.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-01T00:53:44
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



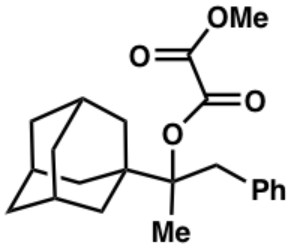
SI-15

Parameter	Value
Data File Name	JYS-1-120-F1-adamantyl-bn-alcohol-clean/ 2/ fid
Title	JYS-1-120-F1-adamantyl-bn-alcohol-clean.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-01T01:08:52
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



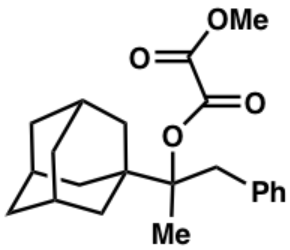
SI-15

Parameter	Value
Data File Name	JYS-1-123-F2-adamantyl-Bn-Me-oxalate-clean/ 1/ fid
Title	JYS-1-123-F2-adamantyl-Bn-Me-oxalate-clean.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-01T01:13:48
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



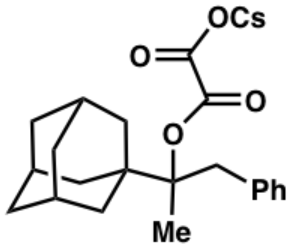
SI-16

Parameter	Value
Data File Name	JYS-1-123-F2-adamantyl-Bn-Me-oxalate-clean/ 2/ fid
Title	JYS-1-123-F2-adamantyl-Bn-Me-oxalate-clean.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-01T01:44:33
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



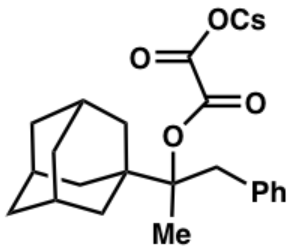
SI-16

Parameter	Value
Data File Name	JYS-1-202/ PROTON01.fid/ fid
Title	PROTON01
Origin	Varian
Solvent	DMSO
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	42
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Acquisition Date	2017-08-09T12:21:55
Spectrometer Frequency	499.65
Spectral Width	8000.0
Nucleus	1H
Acquired Size	24000
Spectral Size	65536



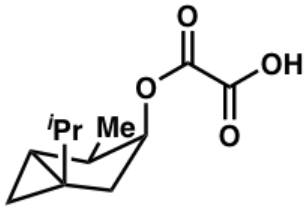
1h

Parameter	Value
Data File Name	JYS-1-202-adamantyl-Bn-Cs-oxalate/ 2/ fid
Title	JYS-1-202-adamantyl-Bn-Cs-oxalate.2.fid
Origin	Bruker BioSpin GmbH
Solvent	DMSO
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-06T23:11:58
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



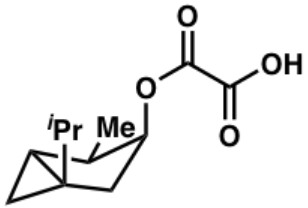
1h

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-60-C/ 1/ fid
Title	DCG-5-60-C.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	176.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-07-25T17:40:58
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



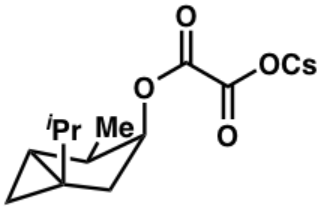
SI-18

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-60-C/ 3/ fid
Title	DCG-5-60-C.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-25T18:14:06
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



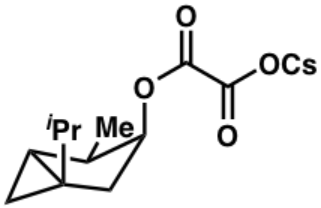
SI-18

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-61-S/ 2/ fid
Title	DCG-5-61-S.2.fid
Origin	Bruker BioSpin GmbH
Solvent	DMSO
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	112.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-07-26T15:29:59
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



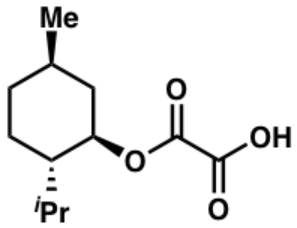
1k

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-61-S/ 4/ fid
Title	DCG-5-61-S.4.fid
Origin	Bruker BioSpin GmbH
Solvent	DMSO
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-26T16:12:22
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



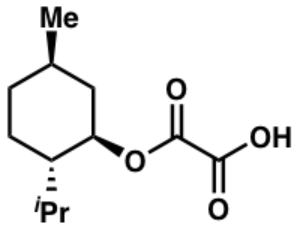
1k

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-180-C/ 1/ fid
Title	DCG-5-180-C.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	176.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-20T19:58:32
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



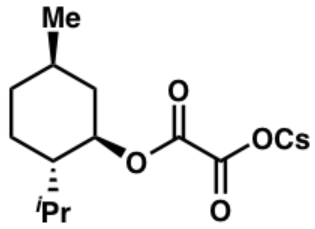
SI-19

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-180-C/ 2/ fid
Title	DCG-5-180-C.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-20T20:14:14
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



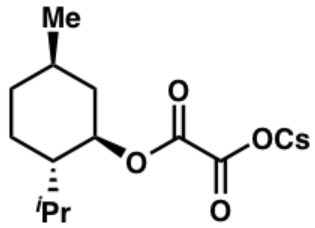
SI-19

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ dgrunenf/ nmr/ DCG-5-181-S/ 1/ fid
Title	DCG-5-181-S.1.fid
Origin	Bruker BioSpin GmbH
Solvent	D2O
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	112.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-21T15:09:13
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

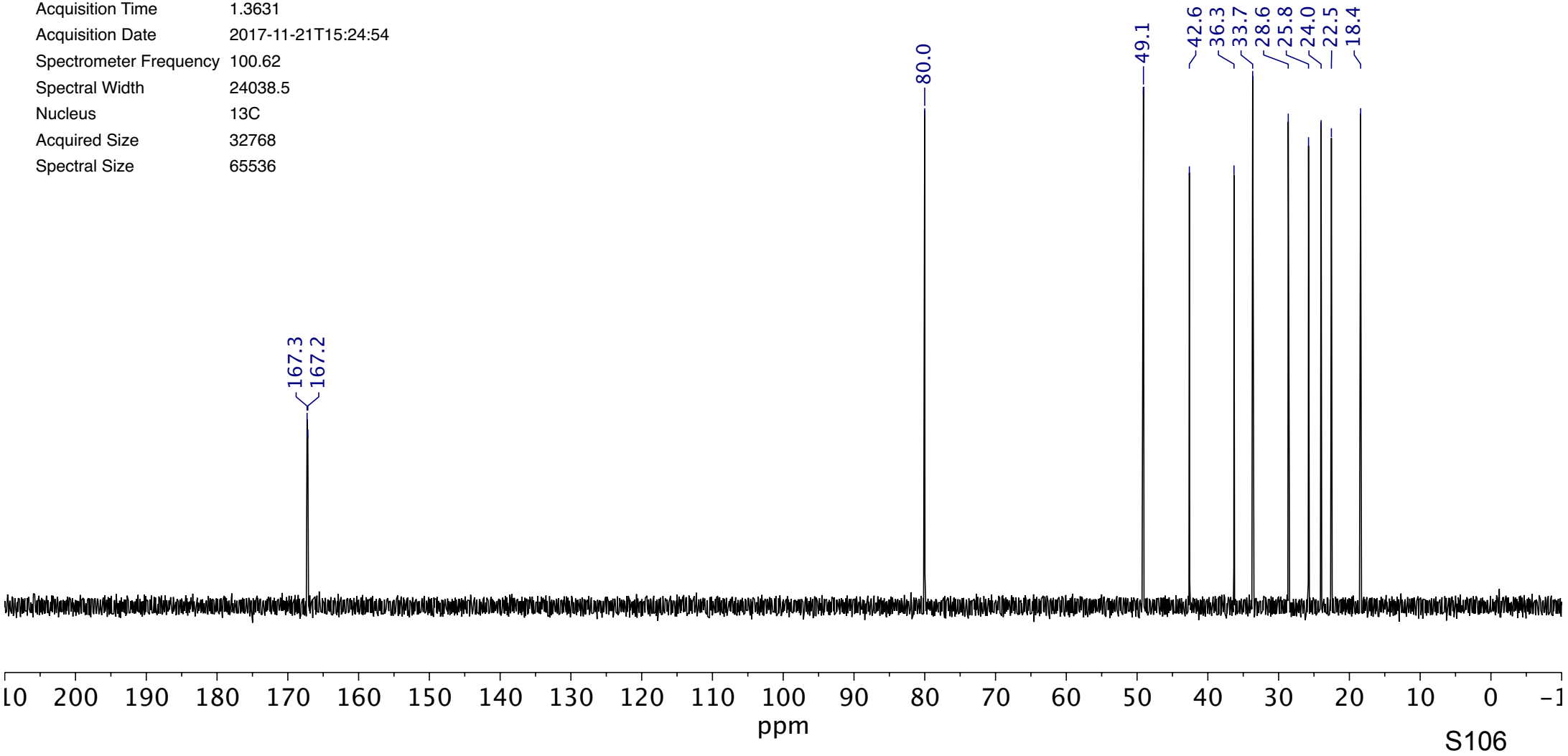


1m

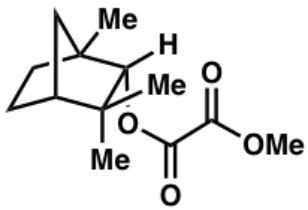
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ dgrunenf/ nmr/ DCG-5-181-S/ 2/ fid
Title	DCG-5-181-S.2.fid
Origin	Bruker BioSpin GmbH
Solvent	D2O
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-21T15:24:54
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



1m

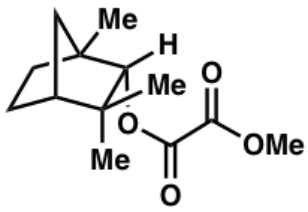


Parameter	Value
Data File Name	JYS-1-180-F1-fenchyl-Me-oxalate/ 1/ fid
Title	JYS-1-180-F1-fenchyl-Me-oxalate.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-04T18:15:04
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



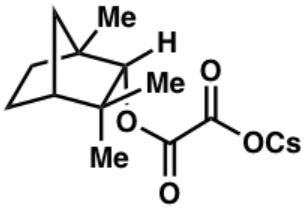
SI-20

Parameter	Value
Data File Name	JYS-1-180-F1-fenchyl-Me-oxalate/ 2/ fid
Title	JYS-1-180-F1-fenchyl-Me-oxalate.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-04T18:44:48
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



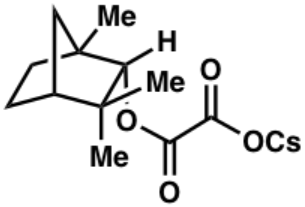
SI-20

Parameter	Value
Data File Name	JYS-1-257-fenchyl-Cs-oxalate/ 1/ fid
Title	JYS-1-257-fenchyl-Cs-oxalate.1.fid
Origin	Bruker BioSpin GmbH
Solvent	DMSO
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	112.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-04T18:49:52
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



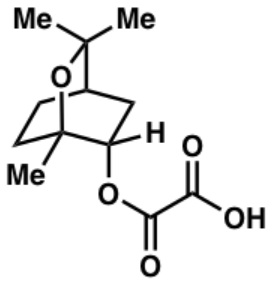
1n

Parameter	Value
Data File Name	JYS-1-257-fenchyl-Cs-oxalate/ 2/ fid
Title	JYS-1-257-fenchyl-Cs-oxalate.2.fid
Origin	Bruker BioSpin GmbH
Solvent	DMSO
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-04T19:20:11
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



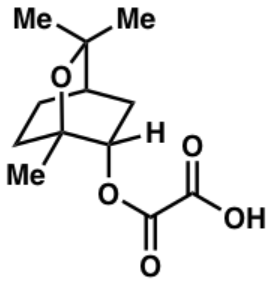
1n

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-160-C/ 1/ fid
Title	DCG-5-160-C.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-03T12:30:06
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



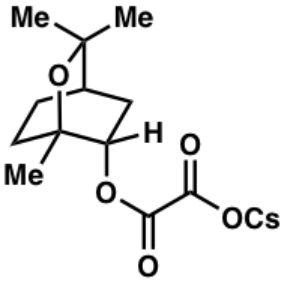
SI-22

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-160-C/ 3/ fid
Title	DCG-5-160-C.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	128
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-03T12:49:51
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



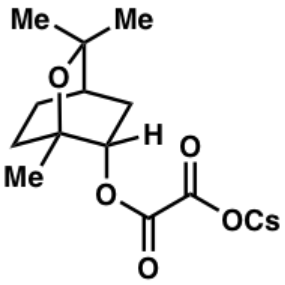
SI-22

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-161-S/ 1/ fid
Title	DCG-5-161-S.1.fid
Origin	Bruker BioSpin GmbH
Solvent	D2O
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	142.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-04T21:05:25
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

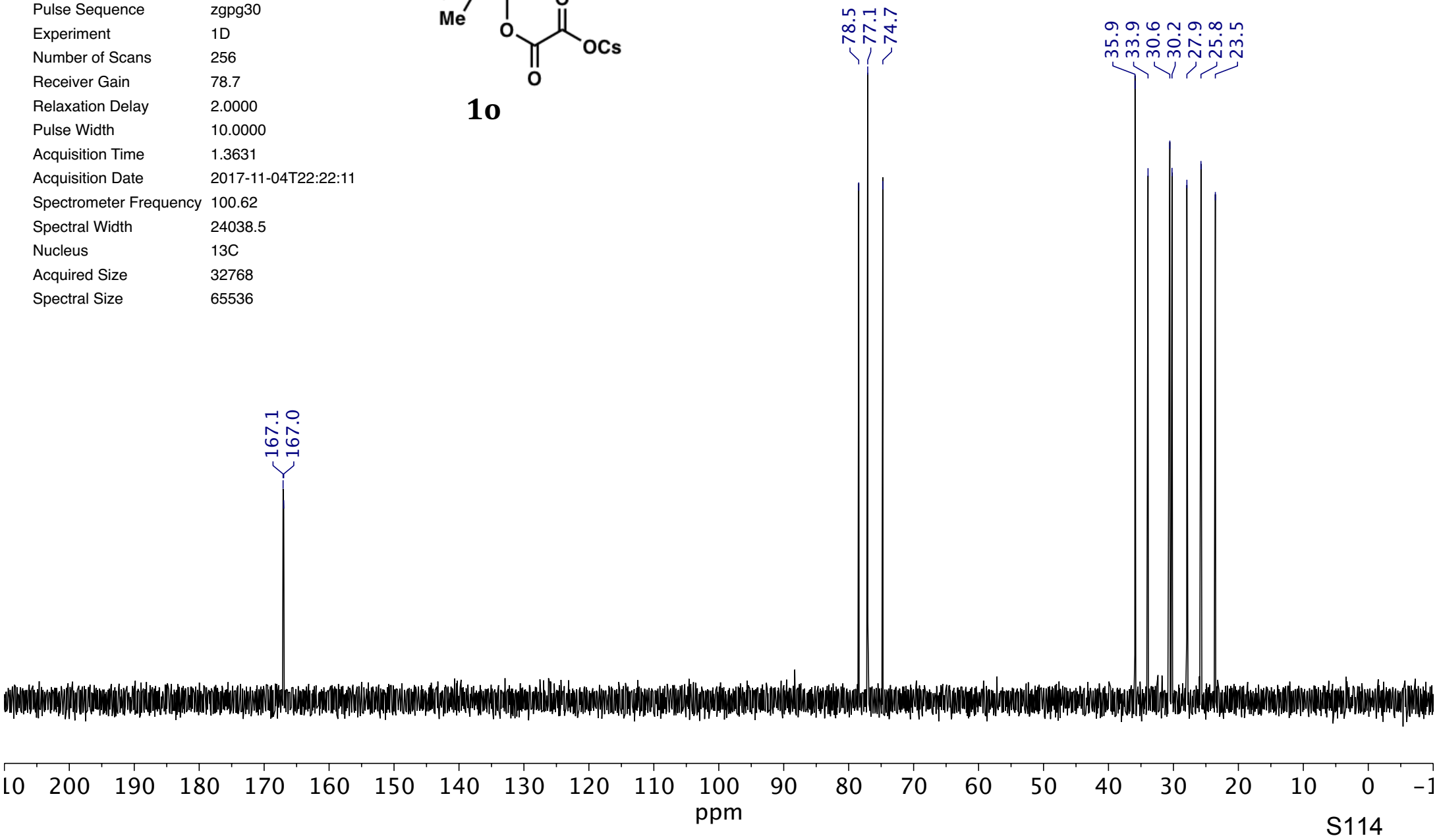


1o

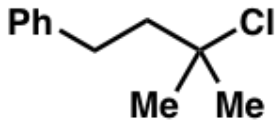
Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-161-S/ 5/ fid
Title	DCG-5-161-S.5.fid
Origin	Bruker BioSpin GmbH
Solvent	D2O
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-04T22:22:11
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



1o

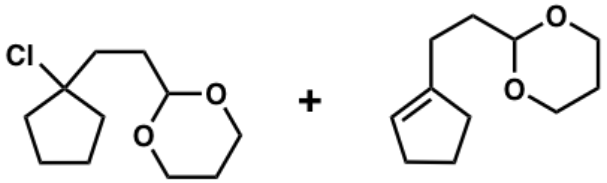


Parameter	Value
Data File Name	JYS-2-205-C-F1-NaOH-model-chloride/1/fid
Title	JYS-2-205-C-F1-NaOH-model-chloride.1.fid
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Acquisition Date	2018-07-14T20:30:57
Spectrometer Frequency	499.64
Spectral Width	8000.0
Nucleus	1H
Acquired Size	24000
Spectral Size	65536



2a

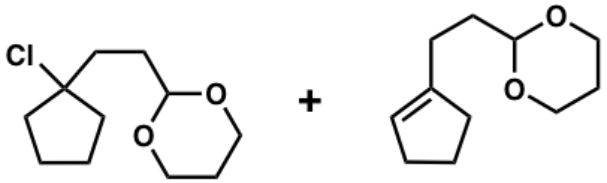
Parameter	Value
Data File Name	JYS-2-185-F1-NaOH-cyclopentyl-acetal-chloride/ 1/ fid
Title	JYS-2-185-F1-NaOH-cyclopentyl-acetal-chloride.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-05-17T05:35:42
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



2b

94 : 6

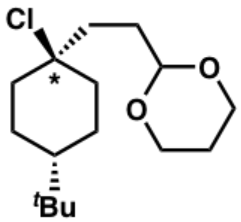
Parameter	Value
Data File Name	JYS-2-185-F1-NaOH-cyclopentyl-acetal-chloride/ 2/ fid
Title	JYS-2-185-F1-NaOH-cyclopentyl-acetal-chloride.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-05-17T06:05:27
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



2b

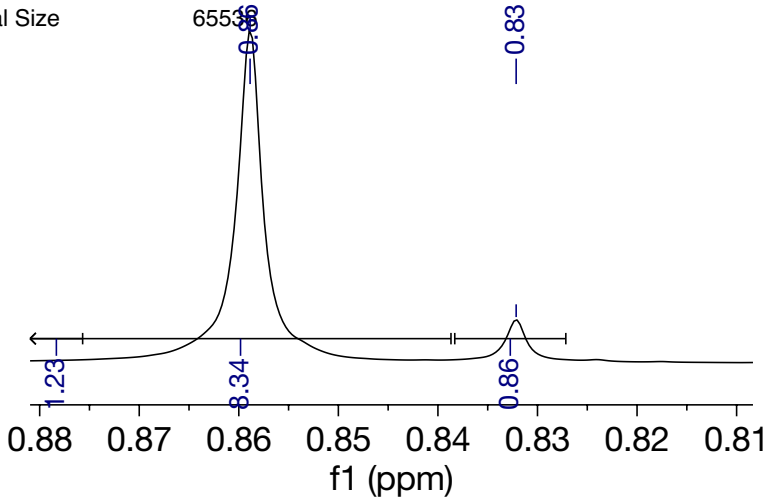
94 : 6

Parameter	Value
Data File Name	JYS-2-127-F1-tbu-cyclohexyl-acetal-chloride/ 1/ fid
Title	JYS-2-127-F1-tbu-cyclohexyl-acetal-chloride.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-04-26T03:13:14
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

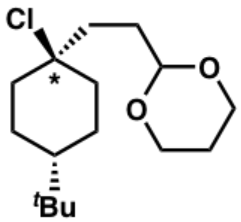


2c

9.8:1 dr

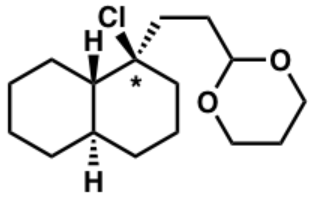


Parameter	Value
Data File Name	JYS-2-127-F1-tbu-cyclohexyl-acetal-chloride/ 2/ fid
Title	JYS-2-127-F1-tbu-cyclohexyl-acetal-chloride.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-04-26T03:43:44
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



2c
9.8:1 dr

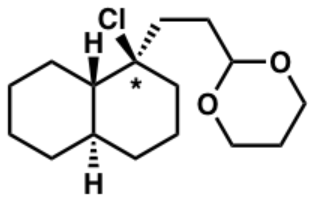
Parameter	Value
Data File Name	JYS-2-147-F1-decalin-acetal-chloride/ 1/ fid
Title	JYS-2-147-F1-decalin-acetal-chloride.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-04-27T01:16:46
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



2d

2.9:1 dr

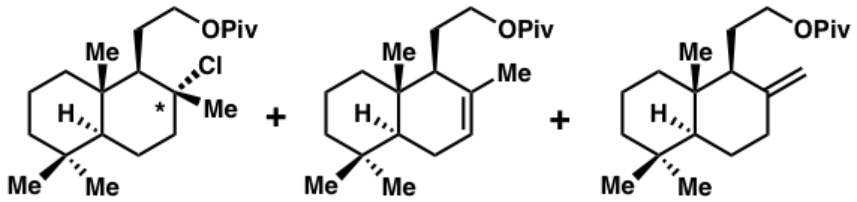
Parameter	Value
Data File Name	JYS-2-147-F1-decalin-acetal-chloride/ 2/ fid
Title	JYS-2-147-F1-decalin-acetal-chloride.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-04-27T01:46:31
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



2d

2.9:1 dr

Parameter	Value
Data File Name	sclareolide-chloride-JYS-2-35-F1/ 1/ fid
Title	JYS-2-35-F1-sclareolide-chloride.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	15.9
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-21T08:55:57
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

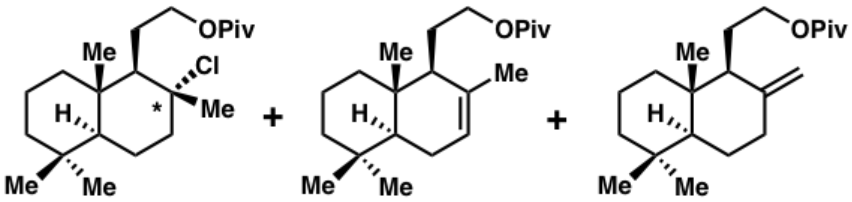


2e **SI-23**

SI-24

92 : 4 : 6 ratio

Parameter	Value
Data File Name	sclareolide-chloride-JYS-2-35-F1/ 2/ fid
Title	JYS-2-35-F1-sclareolide-chloride.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-21T09:26:43
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

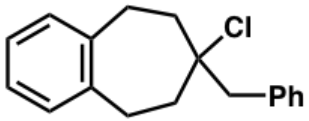


2e **SI-23**

SI-24

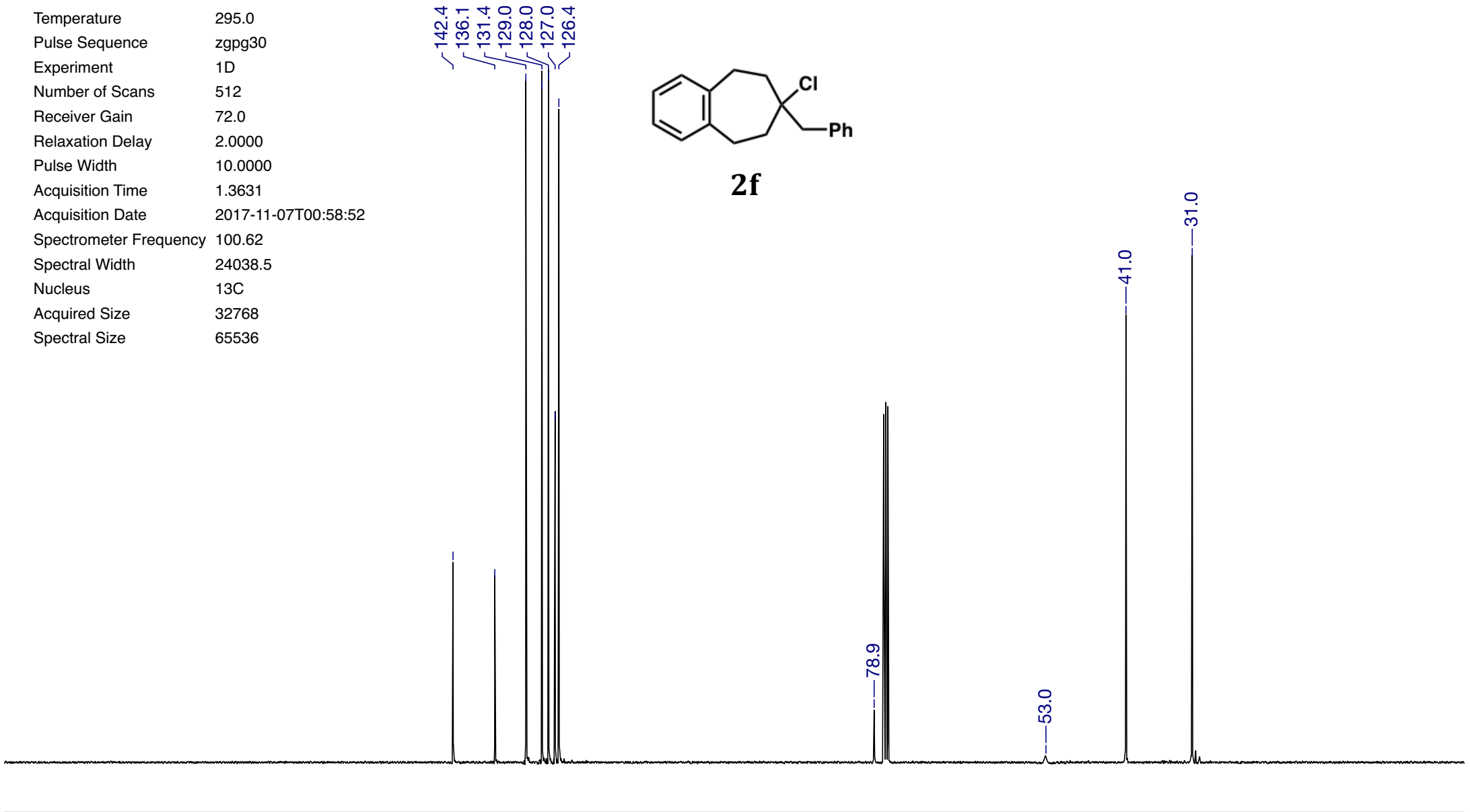
92 : 4 : 6 ratio

Parameter	Value
Data File Name	JYS-1-263-F1-cycloheptyl-Bn-chloride/ 1/ fid
Title	JYS-1-263-F1-cycloheptyl-Bn-chloride.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-07T00:28:34
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



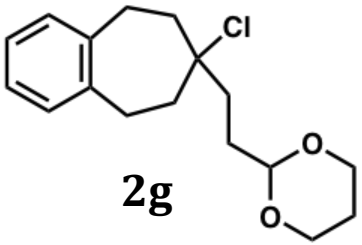
2f

Parameter	Value
Data File Name	JYS-1-263-F1-cycloheptyl-Bn-chloride/ 2/ fid
Title	JYS-1-263-F1-cycloheptyl-Bn-chloride.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-07T00:58:52
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



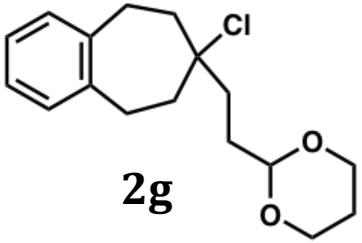
2f

Parameter	Value
Data File Name	JYS-1-208-F2-cycloheptyl-acetal-chloride/ 1/ fid
Title	JYS-1-208-F2-cycloheptyl-acetal-chloride.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-06T23:17:29
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

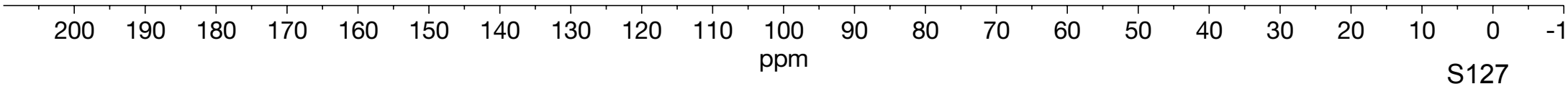


2g

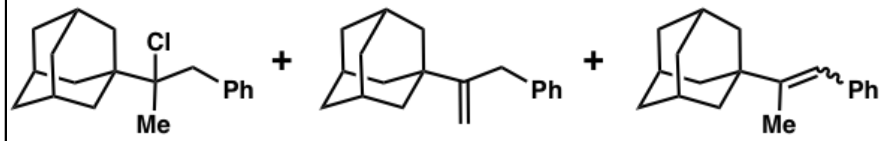
Parameter	Value
Data File Name	JYS-1-208-F2-cycloheptyl-acetal-chloride/ 2/ fid
Title	JYS-1-208-F2-cycloheptyl-acetal-chloride.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-06T23:47:49
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



2g



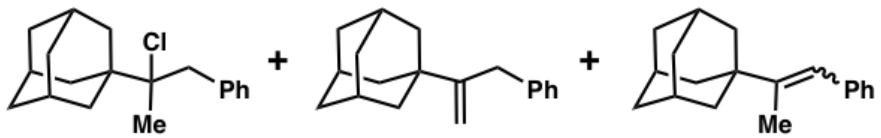
Parameter	Value
Data File Name	adamantyl-bn-chloride-JYS-1-274-F1/ 1/ fid
Title	JYS-1-274-F1-adamantyl-bn-chloride.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-19T20:27:43
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



2h **SI-25**

85 : 8 : 7 ratio

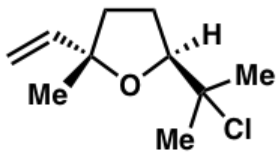
Parameter	Value
Data File Name	adamantyl-bn-chloride-JYS-1-274-F1/ 2/ fid
Title	JYS-1-274-F1-adamantyl-bn-chloride.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-19T20:57:28
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



2h **SI-25**

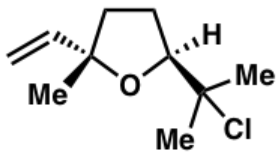
85 : 8 : 7 ratio

Parameter	Value
Data File Name	JYS-2-21-linalool-chloride/ 1/ fid
Title	JYS-2-21-linalool-chloride.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-10-28T19:12:03
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

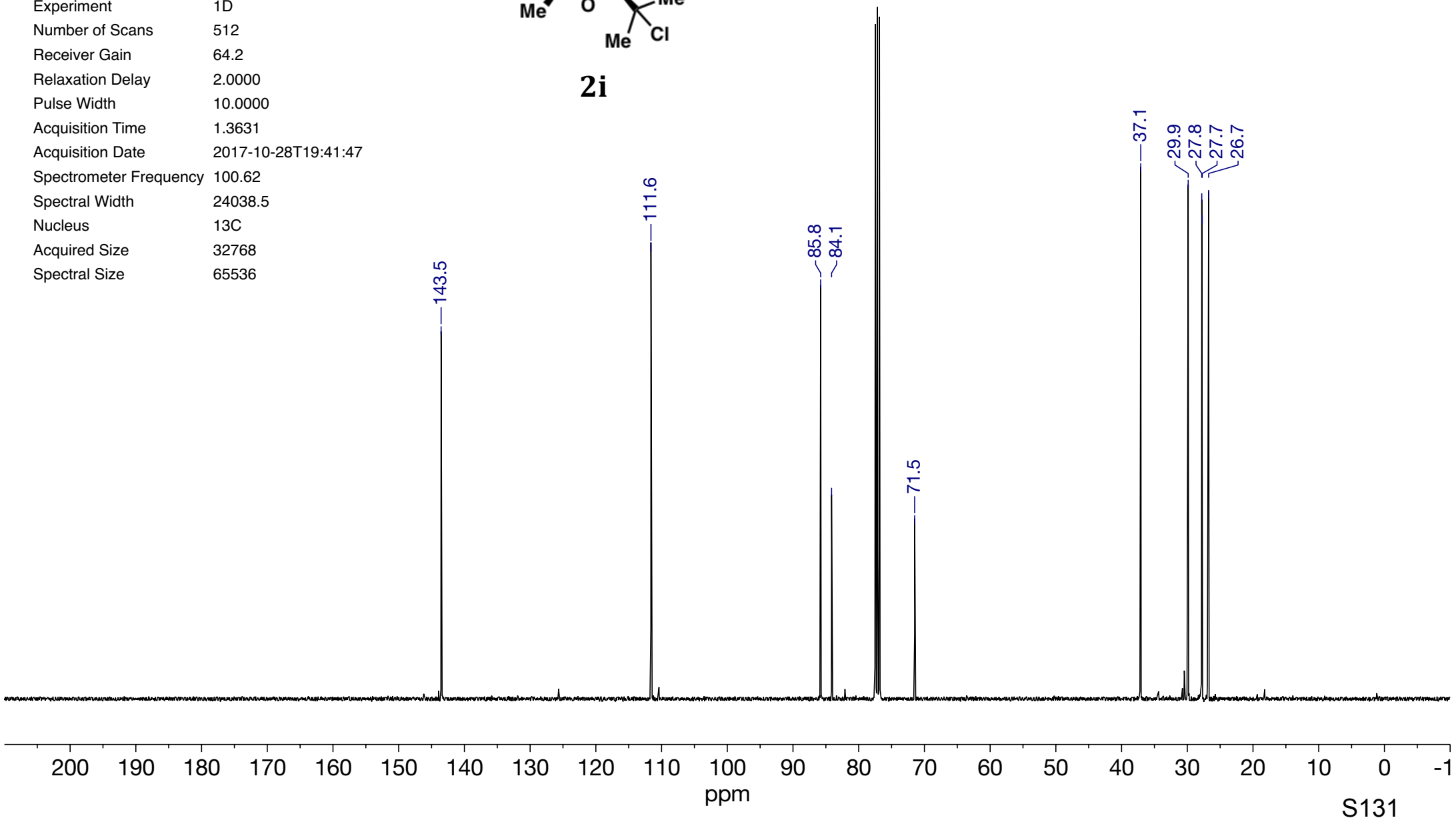


2i

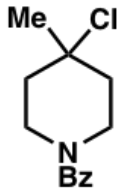
Parameter	Value
Data File Name	JYS-2-21-linalool-chloride/ 2/ fid
Title	JYS-2-21-linalool-chloride.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-10-28T19:41:47
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



2i

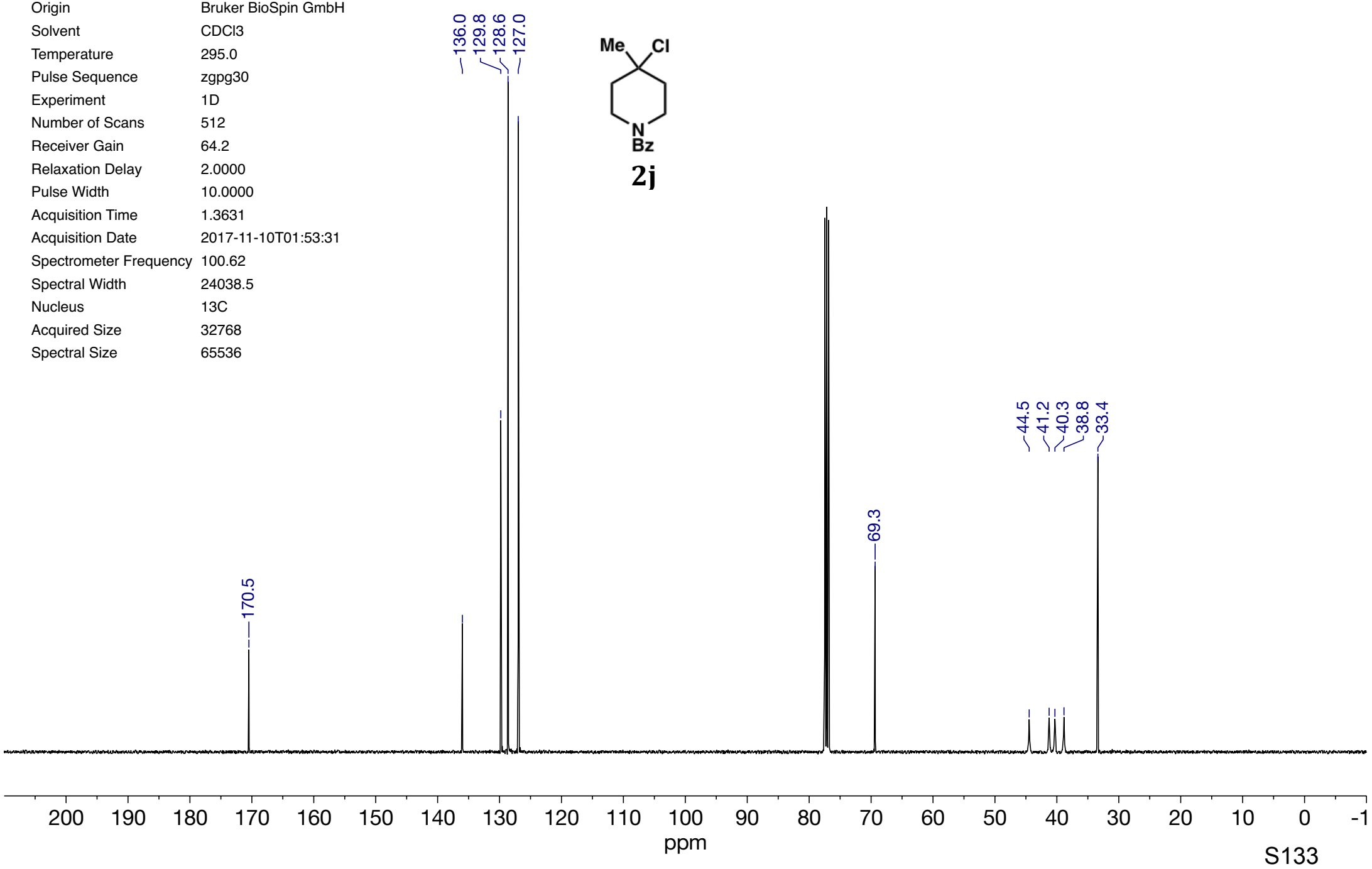


Parameter	Value
Data File Name	Bz-piperidine-chloride-JYS-1-226-F1/ 1/ fid
Title	JYS-1-226-F1-Bz-piperidine-chloride.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-10T01:23:46
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

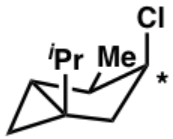


2j

Parameter	Value
Data File Name	Bz-piperidine-chloride-JYS-1-226-F1/ 2/ fid
Title	JYS-1-226-F1-Bz-piperidine-chloride.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-10T01:53:31
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

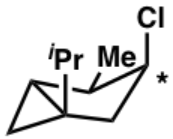


Parameter	Value
Data File Name	thujol-chloride-JYS-1-203-F1/ 1/ fid
Title	JYS-1-203-F1-thujol-chloride.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-19T13:11:11
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



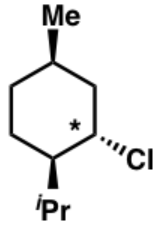
2k
20:1 dr

Parameter	Value
Data File Name	thujol-chloride-JYS-1-203-F1/ 2/ fid
Title	JYS-1-203-F1-thujol-chloride.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-19T13:40:56
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



2k
20:1 dr

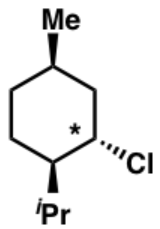
Parameter	Value
Data File Name	isomenthyl-chloride-JYS-1-142-A-F1/ 1/ fid
Title	JYS-1-142-A-F1-isomenthyl-chloride.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-18T08:17:54
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



2l

20:1 dr

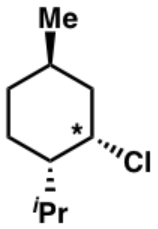
Parameter	Value
Data File Name	isomenthyl-chloride-JYS-1-142-A-F1/ 2/ fid
Title	JYS-1-142-A-F1-isomenthyl-chloride.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-18T08:47:38
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



2l

20:1 dr

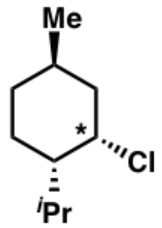
Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-109-1/ 2/ fid
Title	DCG-5-109-1.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	1
Receiver Gain	30.3
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	9.9998
Acquisition Date	2017-09-21T12:28:44
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	80127
Spectral Size	262144



2m

1.5:1 dr

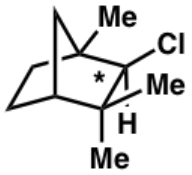
Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-109-1/ 3/ fid
Title	DCG-5-109-1.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	128
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-09-21T12:36:34
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



2m

1.5:1 dr

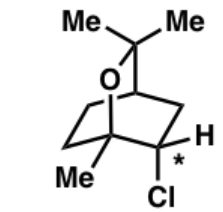
Parameter	Value
Data File Name	JYS-2-36-F1-QNMR/ PROTON01.fid/ fid
Title	PROTON01
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	1
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	5.1000
Acquisition Time	5.0000
Acquisition Date	2017-11-08T15:37:57
Spectrometer Frequency	300.09
Spectral Width	4796.2
Nucleus	1H
Acquired Size	23981
Spectral Size	65536



2n

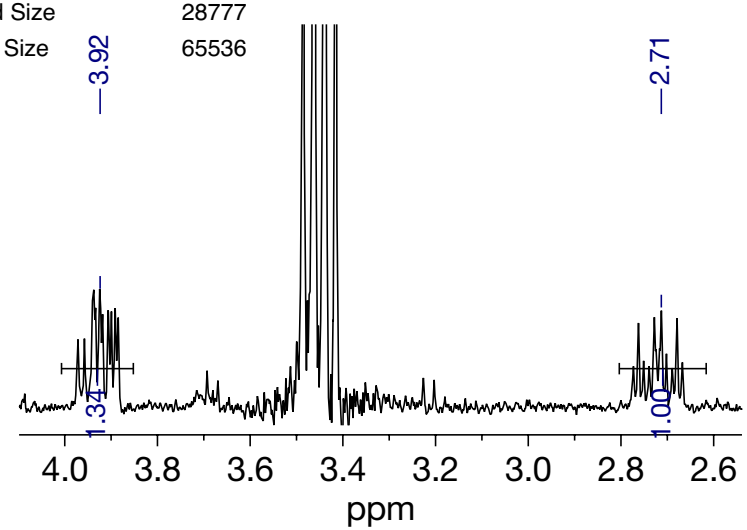
6.7:1 dr

Parameter	Value
Data File Name	JYS-2-50-crude-QNMR/ PROTON01.fid/ fid
Title	PROTON01
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	1
Receiver Gain	0
Relaxation Delay	1.0000
Pulse Width	5.1000
Acquisition Time	6.0000
Acquisition Date	2017-11-20T18:17:50
Spectrometer Frequency	300.09
Spectral Width	4796.2
Nucleus	1H
Acquired Size	28777
Spectral Size	65536



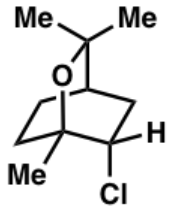
2o

2.9:1 dr



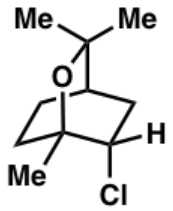
pyrazine standard

Parameter	Value
Data File Name	eucalyptol-chloride-maj-diast-JYS-2-50-F1/ 1/ fid
Title	JYS-2-50-F1-eucalyptol-chloride-maj-diast.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	112.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-28T21:17:36
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



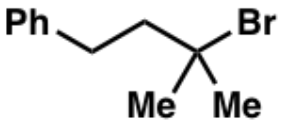
2o
isolated major
diastereomer

Parameter	Value
Data File Name	eucalyptol-chloride-maj-diast-JYS-2-50-F1/ 2/ fid
Title	JYS-2-50-F1-eucalyptol-chloride-maj-diast.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-28T21:47:20
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



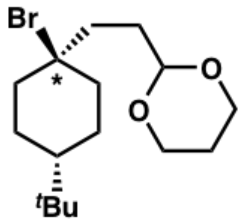
2o
isolated major diastereomer

Parameter	Value
Data File Name	JYS-2-179-C-NaOH-F1-model-bromide/1/fid
Title	JYS-2-179-C-NaOH-F1-model-bromide.1.fid
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Acquisition Date	2018-07-14T20:26:15
Spectrometer Frequency	499.64
Spectral Width	8000.0
Nucleus	1H
Acquired Size	24000
Spectral Size	65536



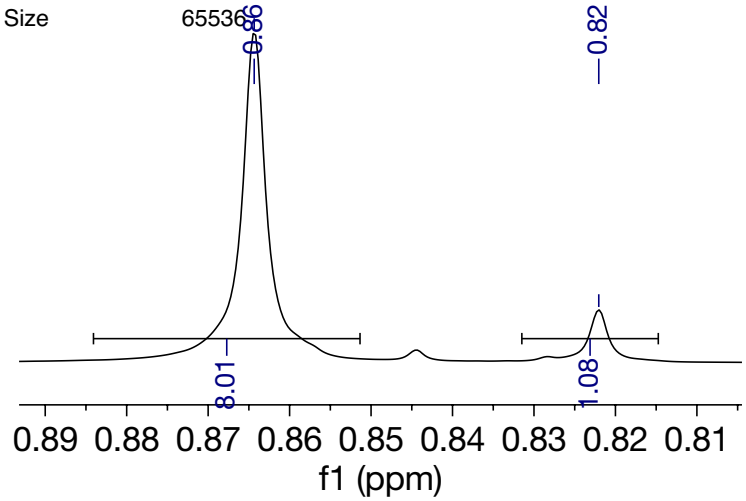
11a

Parameter	Value
Data File Name	JYS-2-200-F1-NaOH-tbu-cy-bromide/ 1/ fid
Title	JYS-2-200-F1-NaOH-tbu-cy-bromide.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-05-14T18:49:47
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

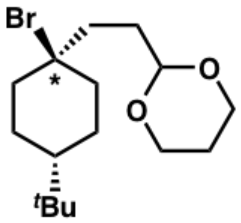


11b

7.4:1 dr



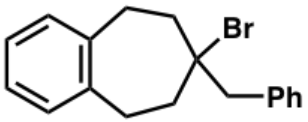
Parameter	Value
Data File Name	JYS-2-200-F1-NaOH-tbu-cy-bromide/ 2/ fid
Title	JYS-2-200-F1-NaOH-tbu-cy-bromide.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	87.8
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-05-14T19:20:18
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



11b

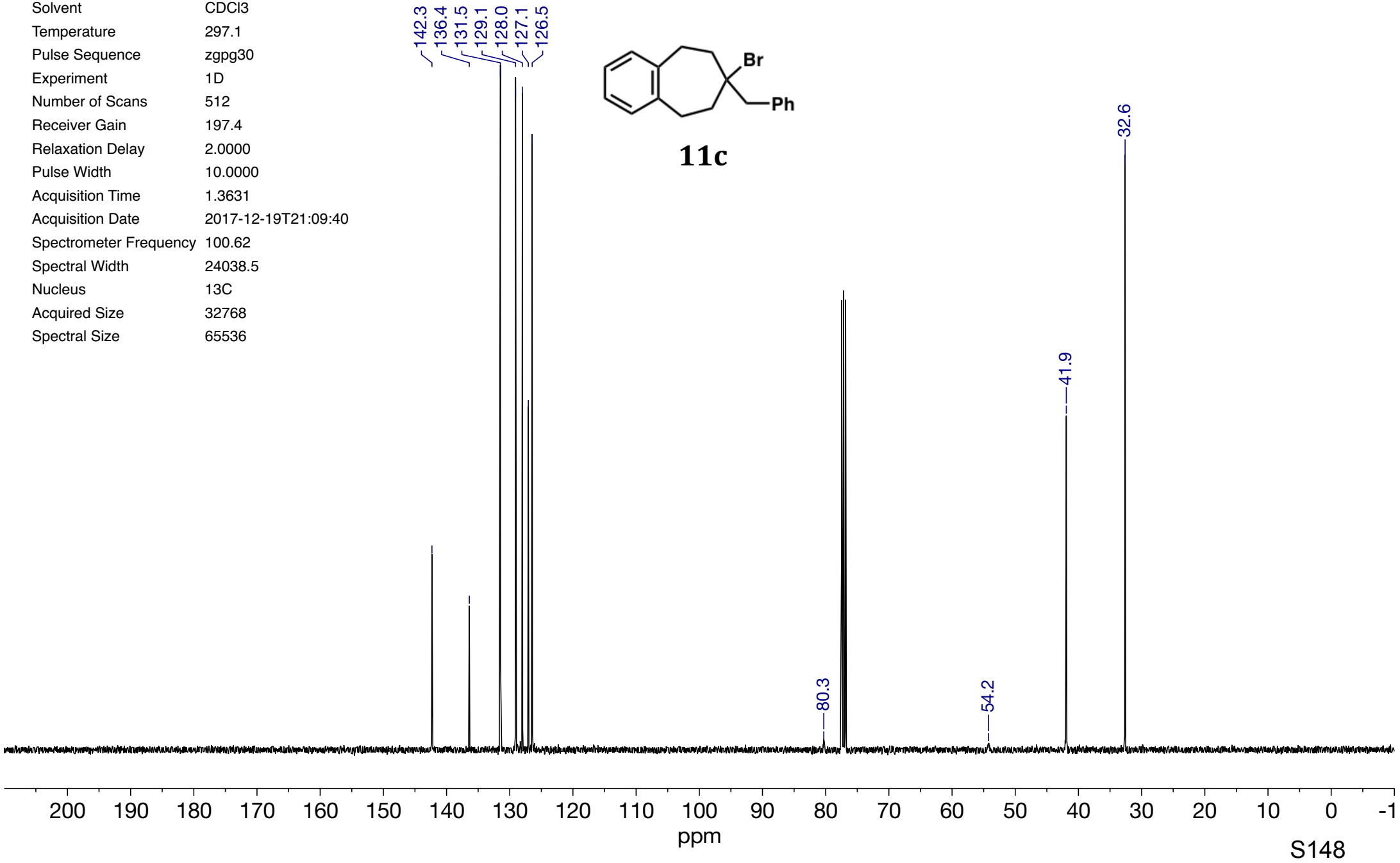
7.4:1 dr

Parameter	Value
Data File Name	cycloheptyl-bn-bromide-JYS-2-62-A-F1/ 1/ fid
Title	JYS-2-62-A-F1-cycloheptyl-bn-bromide.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	8.7000
Acquisition Time	4.0894
Acquisition Date	2017-12-19T20:40:06
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

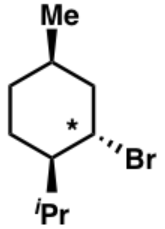


11c

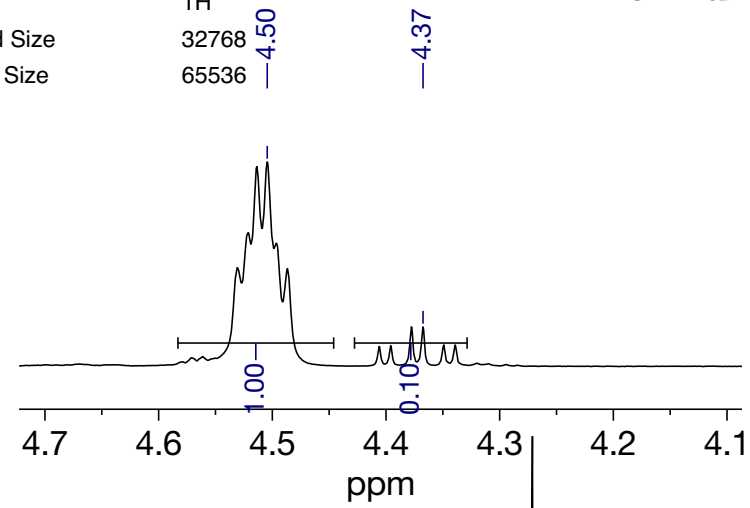
Parameter	Value
Data File Name	cycloheptyl-bn-bromide-JYS-2-62-A-F1/ 2/ fid
Title	JYS-2-62-A-F1-cycloheptyl-bn-bromide.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	197.4
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-12-19T21:09:40
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



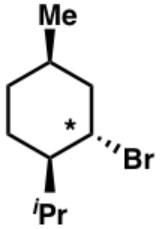
Parameter	Value
Data File Name	isomenthyl-bromide-JYS-2-64-F1/ 1/ fid
Title	JYS-2-64-F1-isomenthyl-bromide.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	8.7000
Acquisition Time	4.0894
Acquisition Date	2017-12-19T21:13:46
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



11d
10:1 dr

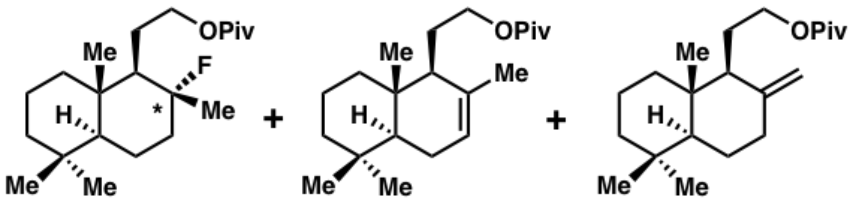


Parameter	Value
Data File Name	isomenthyl-bromide-JYS-2-64-F1/ 2/ fid
Title	JYS-2-64-F1-isomenthyl-bromide.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	197.4
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-12-19T21:43:20
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



11d
10:1 dr

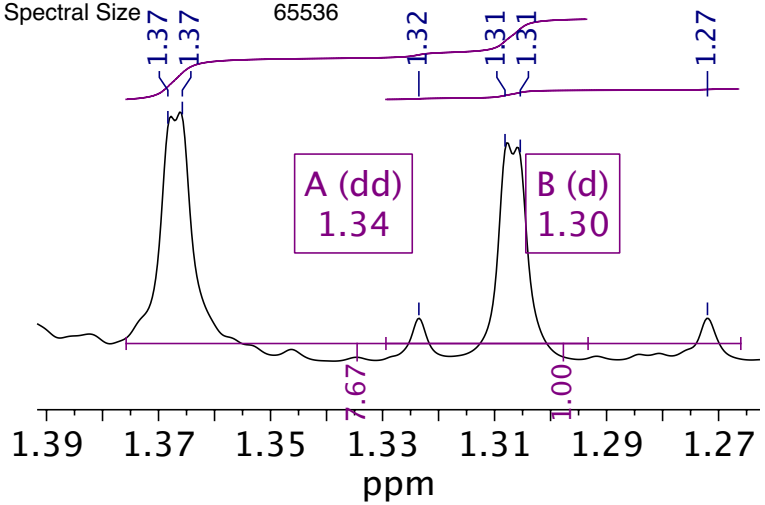
Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-6-28-1/ 1/ fid
Title	DCG-6-28-1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-05-14T20:52:23
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



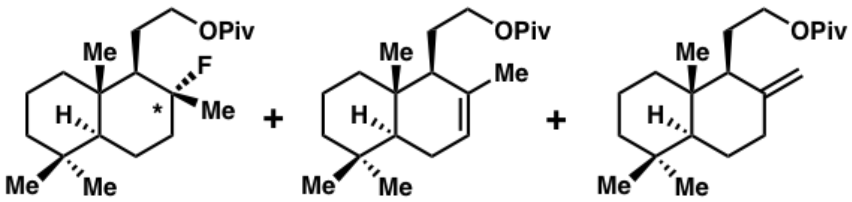
12a **SI-24**

SI-25

89 : 2 : 9 ratio



Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-6-28-1/ 3/ fid
Title	DCG-6-28-1.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	128
Receiver Gain	87.8
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-05-14T21:12:06
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

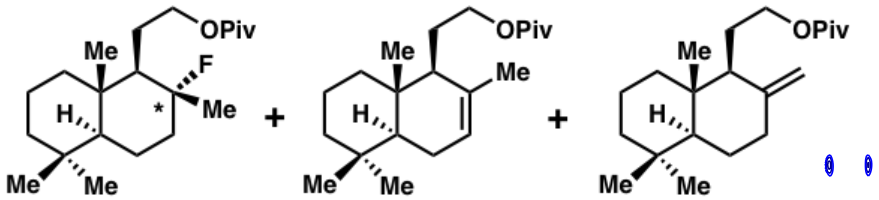


12a **SI-24**

SI-25

89 : 2 : 9 ratio

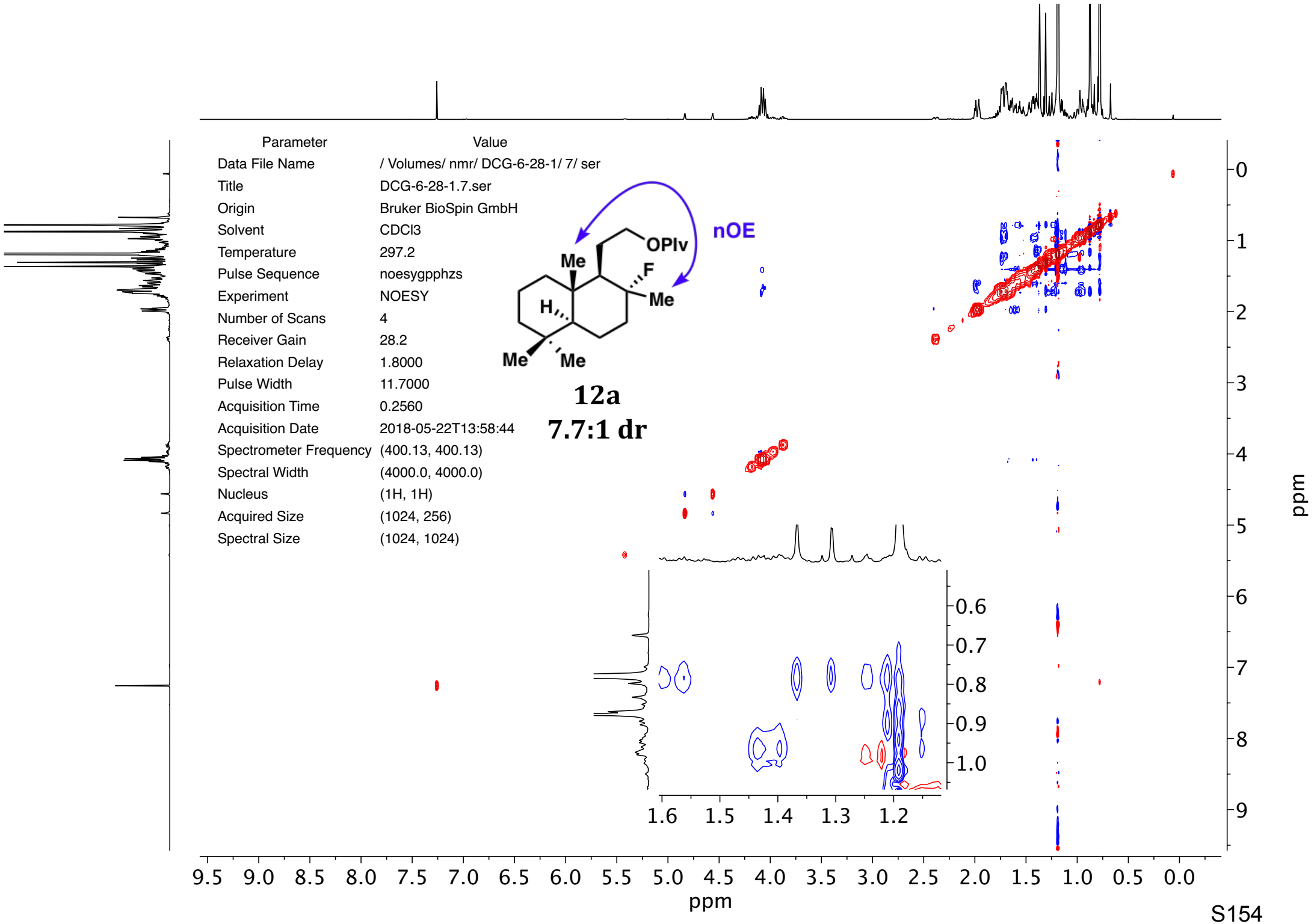
Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-6-28-1/ 2/ ser
Title	DCG-6-28-1.2.ser
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	hsqcedetgpsisp2.4
Experiment	HSQC-EDITED
Number of Scans	2
Receiver Gain	197.4
Relaxation Delay	1.5000
Pulse Width	11.7000
Acquisition Time	0.2135
Acquisition Date	2018-05-14T20:53:40
Spectrometer Frequency	(400.13, 100.62)
Spectral Width	(4795.4, 16611.3)
Nucleus	(1H, 13C)
Acquired Size	(1024, 180)
Spectral Size	(1024, 1024)

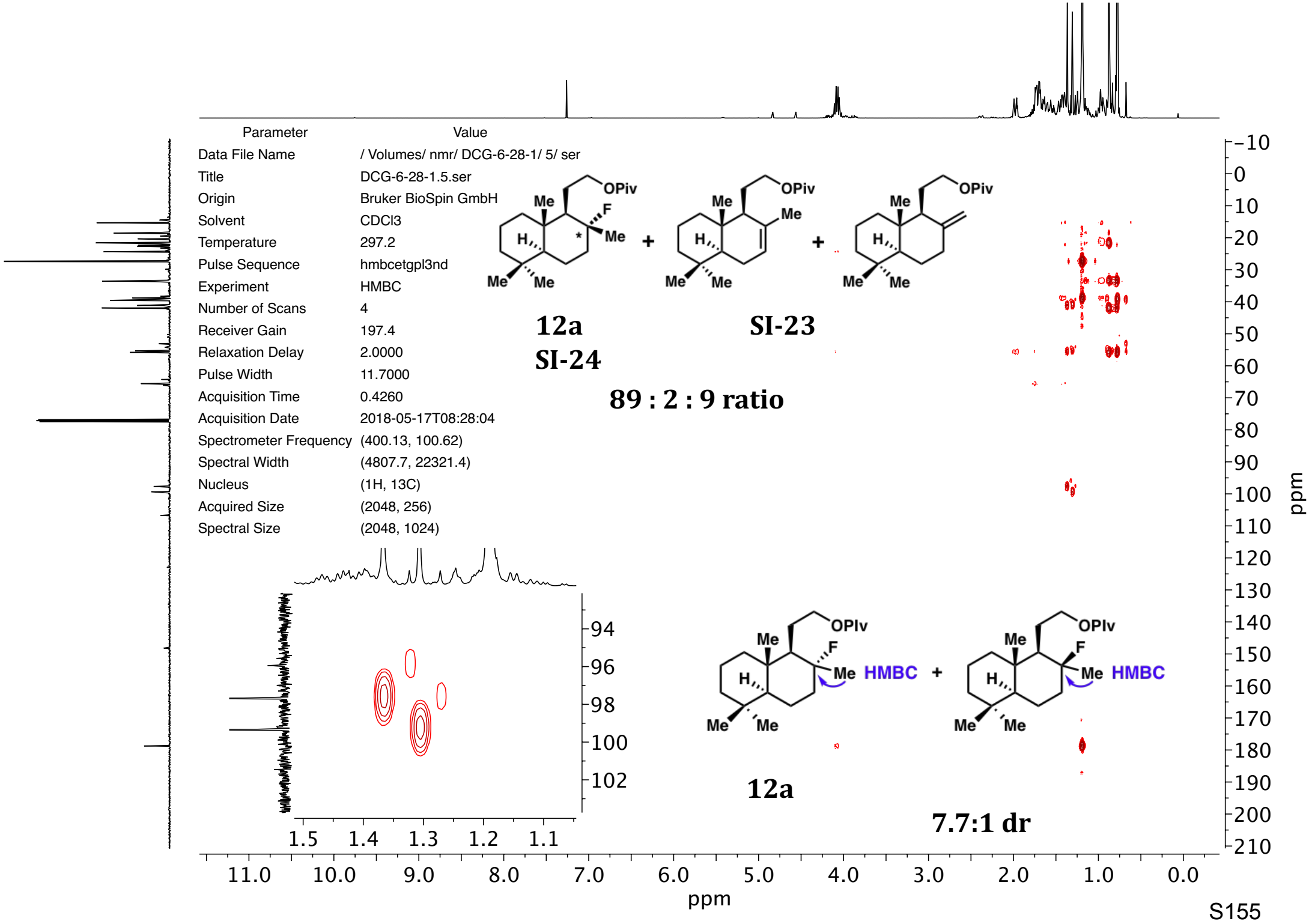


12a **SI-24** **SI-25**

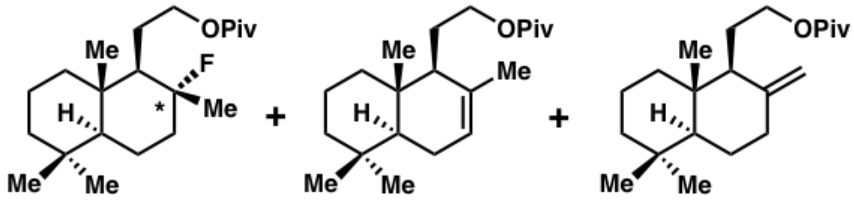
7.7:1 dr

89 : 2 : 9 ratio


Parameter Value
Data File Name / Volumes/ nmr/ DCG-6-28-1/ 7/ ser
Title DCG-6-28-1.7.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence noesygpphzs
Experiment NOESY
Number of Scans 4
Receiver Gain 28.2
Relaxation Delay 1.8000
Pulse Width 11.7000
Acquisition Time 0.2560
Acquisition Date 2018-05-22T13:58:44
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
OPiv
Me
F
Me
H
Me
Me
nOE
12a
7.7:1 dr
ppm
ppm


Parameter Value
Data File Name / Volumes/ nmr/ DCG-6-28-1/ 5/ ser
Title DCG-6-28-1.5.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hmbcetgpl3nd
Experiment HMBC
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 11.7000
Acquisition Time 0.4260
Acquisition Date 2018-05-17T08:28:04
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
12a
SI-23
SI-24
89 : 2 : 9 ratio
12a
HMBC
HMBC
7.7:1 dr
ppm
ppm
S155

Parameter	Value
Data File Name	/ Volumes/ data-1/ DCG-6-28-1-19F.fid/ fid
Origin	Varian
Instrument	vnmrs
Solvent	CDCl3
Temperature	37.0
Experiment	1D
Probe	OneNMR
Number of Scans	32
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	3.2333
Acquisition Time	0.7340
Acquisition Date	2018-05-14T22:07:33
Spectrometer Frequency	376.15
Spectral Width	89285.7
Lowest Frequency	-76618.4
Nucleus	19F

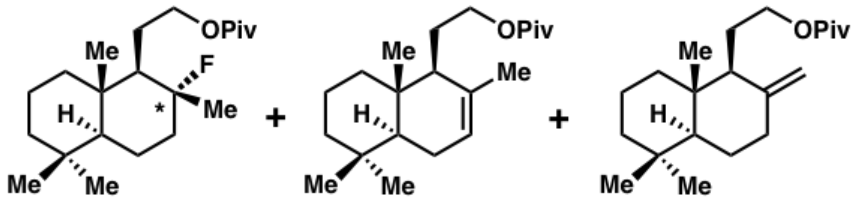


12a **SI-23**

SI-24

89 : 2 : 9 ratio

Parameter	Value
Data File Name	/ Volumes/ data/ DCG-6-28-1-F-C-HSQC--118ppm.fid/ fid
Title	DCG-6-28-1-F-C-HSQC--118ppm
Origin	Varian
Solvent	CDCl3
Temperature	50.0
Pulse Sequence	HSQCAD
Experiment	HSQC
Number of Scans	16
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	9.7000
Acquisition Time	0.1500
Acquisition Date	2018-05-22T15:33:22
Spectrometer Frequency	(376.14, 100.54)
Spectral Width	(9842.5, 20105.6)
Nucleus	(19F, 13C)
Acquired Size	(1476, 128)
Spectral Size	(2048, 1024)

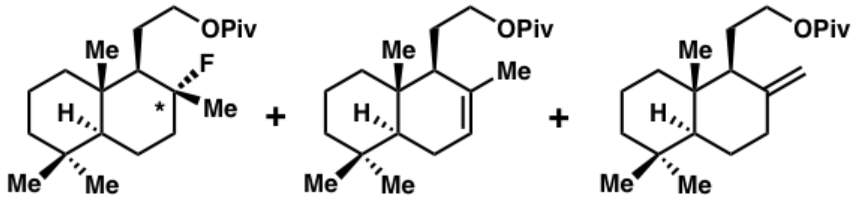


12a **SI-23**

SI-24

89 : 2 : 9 ratio

Parameter	Value
Data File Name	/ Volumes/ data/ DCG-6-28-1-F-C-HSQC.fid/ fid
Title	DCG-6-28-1-F-C-HSQC
Origin	Varian
Solvent	CDCl3
Temperature	50.0
Pulse Sequence	HSQCAD
Experiment	HSQC
Number of Scans	16
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	9.7000
Acquisition Time	0.1500
Acquisition Date	2018-05-18T22:00:49
Spectrometer Frequency	(376.12, 100.54)
Spectral Width	(9842.5, 20105.6)
Nucleus	(19F, 13C)
Acquired Size	(1476, 128)
Spectral Size	(2048, 1024)

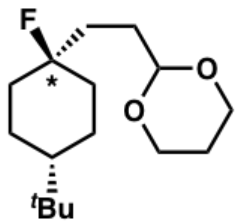


12a **SI-23**

SI-24

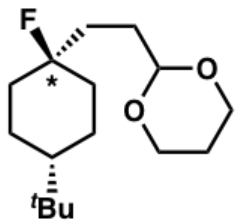
89 : 2 : 9 ratio

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-6-29-1/ 1/ fid
Title	DCG-6-29-1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-05-14T20:27:06
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



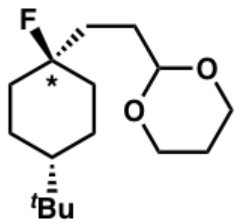
12b
3:1

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-6-29-1/ 3/ fid
Title	DCG-6-29-1.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	128
Receiver Gain	64.2
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-05-14T20:46:53
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



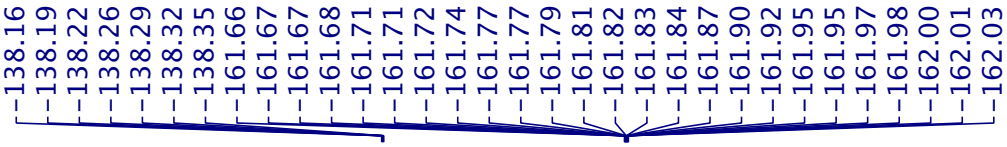
12b
3:1

Parameter	Value
Data File Name	/ Volumes/ data/ DCG-6-29-1-19F.fid/ fid
Title	DCG-6-29-1-19F
Origin	Varian
Solvent	CDCl3
Temperature	37.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	32
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	3.2333
Acquisition Time	0.7340
Acquisition Date	2018-05-14T22:03:20
Spectrometer Frequency	376.15
Spectral Width	89285.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

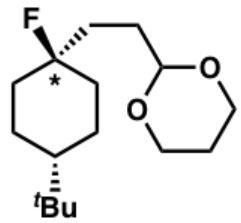


12b

3:1



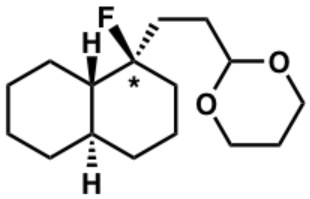
Parameter	Value
Data File Name	/ Volumes/ data-1/ DCG-6-29-1-F-C-HSQC.fid/ fid
Title	DCG-6-29-1-F-C-HSQC
Origin	Varian
Solvent	CDCl3
Temperature	37.0
Pulse Sequence	HSQCAD
Experiment	HSQC
Number of Scans	16
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	9.7000
Acquisition Time	0.1500
Acquisition Date	2018-05-16T22:11:52
Spectrometer Frequency	(376.13, 100.54)
Spectral Width	(9842.5, 20105.6)
Nucleus	(19F, 13C)
Acquired Size	(1476, 128)
Spectral Size	(2048, 1024)



12b

3:1

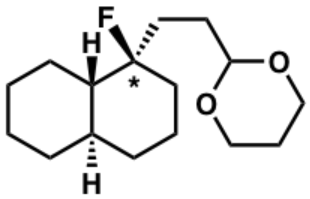
Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-6-36-A-1/ 1/ fid
Title	DCG-6-36-A-1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-05-16T13:20:04
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



12c

1.25:1 dr

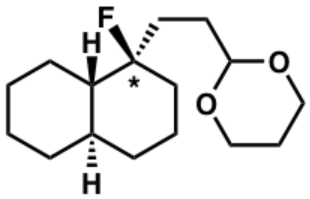
Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-6-36-A-1/ 3/ fid
Title	DCG-6-36-A-1.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-05-16T13:47:07
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



12c

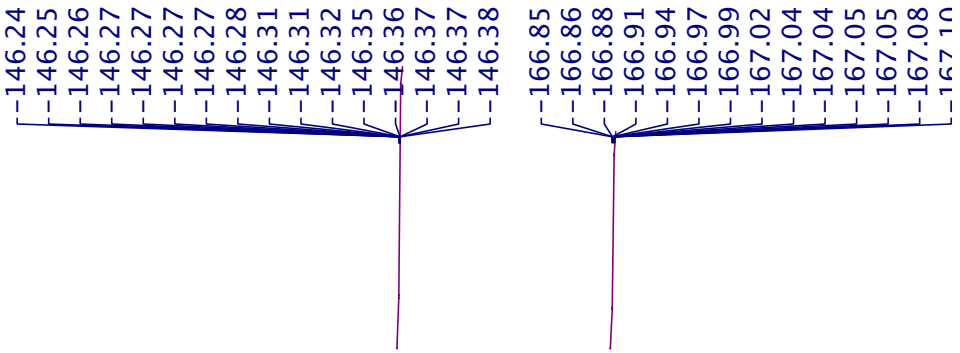
1.25:1 dr

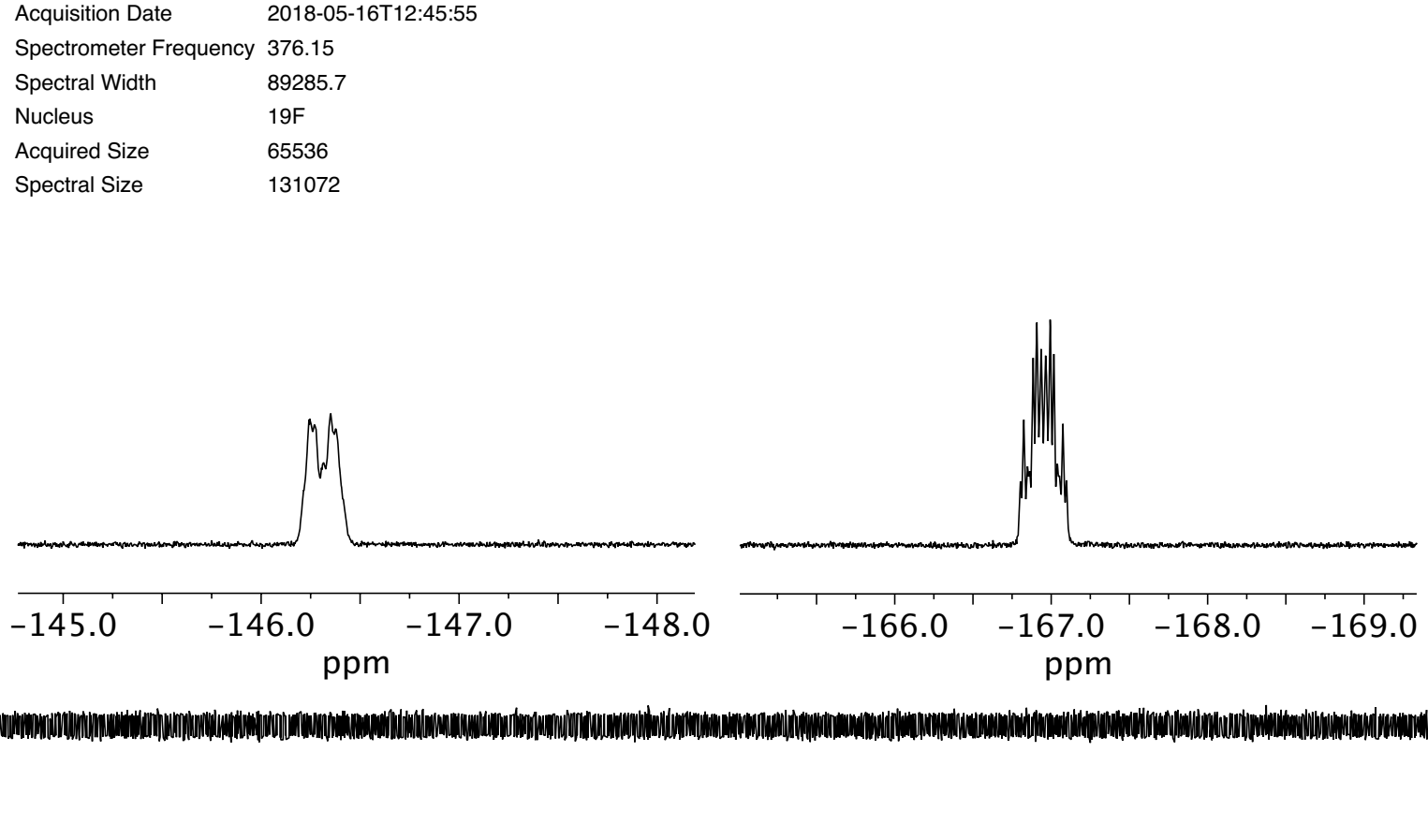
Parameter	Value
Data File Name	/ Volumes/ data-1/ DCG-6-36-A-1-19F.fid/ fid
Title	DCG-6-36-A-1-19F
Origin	Varian
Solvent	CDCl3
Temperature	37.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	3.2333
Acquisition Time	0.7340
Acquisition Date	2018-05-16T12:45:55
Spectrometer Frequency	376.15
Spectral Width	89285.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072



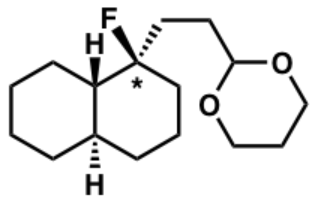
12c

1.25:1 dr





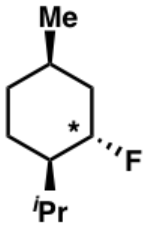
Parameter	Value
Data File Name	/ Volumes/ data-1/ DCG-6-36-A-1-F-C-HSQC.fid/ fid
Title	DCG-6-36-A-1-F-C-HSQC
Origin	Varian
Solvent	CDCl3
Temperature	37.0
Pulse Sequence	HSQCAD
Experiment	HSQC
Number of Scans	16
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	9.7000
Acquisition Time	0.1500
Acquisition Date	2018-05-16T21:14:03
Spectrometer Frequency	(376.12, 100.54)
Spectral Width	(9842.5, 20105.6)
Nucleus	(19F, 13C)
Acquired Size	(1476, 128)
Spectral Size	(2048, 1024)



12c

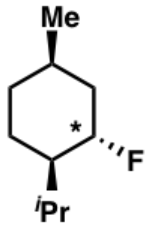
1.25:1 dr

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-302-1/ 2/ fid
Title	DCG-5-302-1.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	127.1
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2018-05-04T15:14:50
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



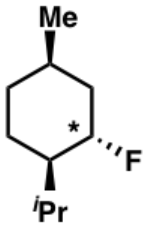
12d
10.7:1 dr

Parameter	Value
Data File Name	/ Volumes/ nmr/ DCG-5-302-1/ 4/ fid
Title	DCG-5-302-1.4.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-05-04T15:56:31
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



12d
10.7:1 dr

Parameter	Value
Data File Name	/ Volumes/ data-1/ DCG-5-302-1-19F.fid/ fid
Title	DCG-5-302-1-19F
Origin	Varian
Solvent	CDCl3
Temperature	37.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	32
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	3.2333
Acquisition Time	0.7340
Acquisition Date	2018-05-03T15:40:37
Spectrometer Frequency	376.15
Spectral Width	89285.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072



12d

10.7:1 dr